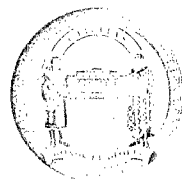
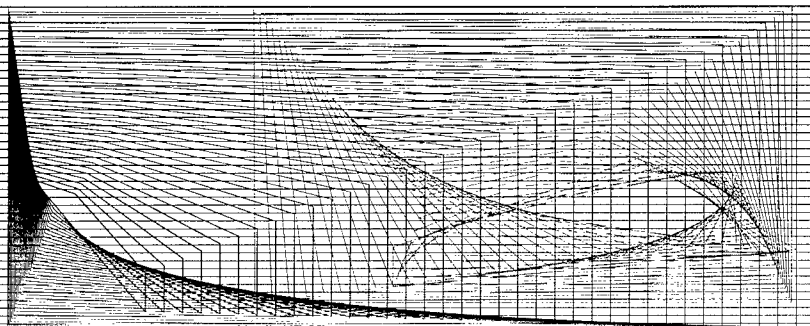


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FORMATION OF THE CURRENT THROUGH ORGANIC MOLECULES WITH STRONGLY SEPARATED ENERGY LEVELS

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A theoretical description of the current formation in the device "electrode L-molecule-electrode R" (LMR) is carried out for a special type of molecules with strongly separated energy levels. These levels can appear if a molecule contains either incorporated metallic ions or/and double/triple chemical bonds connected by saturated chemical bonds. It is shown that in the preresonant voltage region, the current is formed as an additive sum of the partial currents associated with an electron transmission through each separated level. Current-voltage characteristics manifest the absence of any correlation among different electron transfer pathways. Situation changes essentially at such applied voltages when one of the levels becomes isoenergetic to the Fermi-level of one of the electrodes. In this case, a resonant transmission through the level is established and thus, owing to inelastic hopping processes between the electrodes and the molecule, a resonant level is populated by the transferred electrons. The probability of this population is defined by relation between the incoming and outgoing hopping rates. Since a resonant occupation of the molecular level by an extra electron leads to a molecular charging the transmission of other electrons either through already occupied level or through the empty levels proceeds on the background of a Coulomb repulsion between already captured electron and the transferred electrons. Thus, a current formation exhibits an essential modification when a resonant transmission regime is switched on in the LMR device, even though the levels are well energetically separated. The main result of our study is that a combined action of a kinetic charging of the molecule and a Coulomb repulsion between the electrons captured by the molecule in the course of charge transmission is an important factor controlling the current formation. The combined effect appears even though only a single molecular level is involved into a resonant transmission process. Moreover, if a kinetic charging of the molecule depends on direction of the applied external electric field a specific kinetic rectification effect appears for the current [1,2,3].

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PHOTODYNAMICS OF OLED TRIPLET EMITTERS

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The phosphorescent OLED materials cyclometalated *fac* tris(2-phenylpyridine) iridium(III) [Ir(ppy)₃] and platinum-octaethyl-porphyrin (PtOEP) were characterized by absorption and emission spectroscopic methods [1-3]. Neat films, doped films, and organic solutions were investigated. The host materials for the doped films were polystyrene (PS), 4,4'-N,N'-dicarbazole-biphenyl (CBP), and N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD). For organic solutions the solvents tetrahydrofuran (THF), toluene, and chloroform were used. The absorption cross-section spectra including singlet-triplet absorption, the triplet-singlet stimulated emission cross-section spectra, the phosphorescence quantum distributions, the phosphorescence quantum yields, and the phosphorescence signal decays were determined. In neat films of Ir(ppy)₃ a luminescence self-quenching occurs (emission quantum yield $\phi_L \approx 0.01$, emission lifetime $\tau_L \approx 15$ ns). In the neat film of PtOEP a red-shifted excimer luminescence is observed ($\phi_L \approx 0.018$, $\tau_L \approx 1.9$ ns). In doped films (PS, CBP, TPD) as well as in de-aerated liquid solutions (THF, toluene, chloroform) high phosphorescence quantum yields are obtained (up to 90 % for Ir(ppy)₃ in PS, up to 60 % for PtOEP in de-aerated PS). In air-saturated films, and more strongly in liquid solutions, the phosphorescence efficiency is reduced by oxygen quenching according to $^3D^* + ^3O_2 \rightarrow ^1D + ^1O_2^*$. At intense short-pulse laser excitation the phosphorescence lifetime is shortened by triplet-triplet annihilation according to $^3D^* + ^3D^* \rightarrow ^1D + ^1D \rightarrow ^3D^* + ^1D$ [1].

In the case of ground-state depopulation by intense short-pulse laser excitation no amplification of spontaneous emission was observed (no possible laser action) indicating higher triplet-triplet excited-state absorption cross-section than triplet-singlet stimulated emission cross-section [1].

Excitation of Ir(ppy)₃ and PtOEP doped TPD films in the absorption region of the TPD host causes Förster-type singlet-singlet energy transfer from host to guest ($^1H^* + ^1G \rightarrow ^1H + ^1G^*$) followed by singlet-triplet intersystem crossing in the guest system ($^1G^* \rightarrow ^3G^*$) and phosphorescence emission of the guests. Temperature dependent phosphorescence studies revealed Dexter-type ($T_1(\text{dye}_1) + S_0(\text{dye}_2) \leftrightarrow T_1(\text{dye}_2) + S_0(\text{dye}_1)$) triplet-triplet exothermic forward excitation transfer from $^3\text{Ir(ppy)}_3$ to ^3TPD and endothermic back-transfer from ^3TPD to $^3\text{Ir(ppy)}_3$. The experimental results are compatible with Dexter-type exothermic triplet-triplet forward excitation transfer from ^3TPD to $^3\text{PtOEP}$ [2]. In a TPD film doped with

Ir(ppy)₃ and PtOEP strong quenching of the Ir(ppy)₃ luminescence indicated Dexter-type excitation transfer from ³Ir(ppy)₃ to ³PtOEP [3].

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PHOTO-SWITCHABLE TRAPS FOR CHARGE CARRIERS – A RESUMÉ

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Transport of charge carriers in molecular materials is often controlled by local states (traps) formed by chemical and/or structural defects. The energetics of the trap formation can be qualitatively explained within a model [1,2] based on the electrostatic approach developed by Lyons [3]. According to the model, the energy of a state allowed for a carrier localized on a molecule is a superposition of a molecular parameter (ionization energy or electron affinity) and a contribution from electrostatic interactions between the localized carrier and surrounding polarizable molecules (polarization energy). A suitable local modification of any of these parameters results in a formation of traps for electrons and/or holes.

The electrostatic model can also be employed to simulate the situation often encountered in low-molecular weight materials and polymers, where polar species are dispersed in non-polar matrices. Suitable calculations [4,5] have demonstrated that traps as deep as ca. 0.4-0.5 eV can appear on sites adjacent to a polar molecule though the molecule itself does not necessarily form the trap. Both the depths and the cross sections of the traps formed in such a way were found to depend on the dipole moment. Independently, the same species can form chemical traps provided their ionization energies and/or electron affinities fulfil the relations given in [1]. These features offer a possibility of controlling the trap depths (and hence the carrier mobilities) by a modulation of the dipole moments of the dopants (e.g., by light). If the species responsible for the formation of traps can be switched between two structures differing in their dipole moments and/or positions of HOMO and LUMO levels, then such materials can act as molecular switches performing their action on both microscopic and macroscopic level [6-8].

The contribution will summarize results of model calculations performed on molecular systems, employing both, the classical electrostatic model [4-6], and *ab initio* quantum chemical calculations [8]

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METASTABLE CHARGED STATES IN CONJUGATED POLYMERS

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Metastable charged states are known to have several negative effects on electronic devices based on organic materials in general and conjugated polymers in particular. Charge carriers (polarons) and coulombically bound polaron pairs, stabilized by trapping, can efficiently quench excitons, which imposes a serious limitation on quantum yield of electroluminescence in an organic light-emitting diode. Localization of charges in the channel of an organic thin-film transistor (TFT) permanently screens the gate potential and thereby caused instability and/or degradation of the device characteristics. Recent studies of the bias-stress effect in the channel of polymer TFTs [1], have revealed (1) an unusually small cross-section of hole localization, which results in low rate of charge accumulation, and (2)

increasing localization rate per unit carrier at higher hole densities in the channel resembling a bimolecular process. In TFTs, the bias-stress effect typically develops slowly when the transistor is turned on for an extended time and this effect is usually reversible although annealing is sometimes required to fully recover the unstressed state. It has been shown that conventional trapping is generally too fast to account for the stress effect because equilibrium density of trapped carriers has to be established by the time at which the conductive channel is formed

In the present report we show that a charged trion [2], consisting of two on-chain polarons of the same sign (e.g. positive polarons) and a trapped polaron of the opposite sign (e.g. deeply trapped electron) can be metastable with respect to both dissociation and recombination. A trion can be created upon fusion of a free polaron with a neutral pair, which eliminates a high Coulomb potential barrier for fusion of two charge carriers into a bipolaron. We argue that trions can be created by photoexcitation of a conjugated polymer in which illumination creates a high density of geminate pairs. Since a metastable trion is anchored by a deeply trapped charge it is immobile and can be considered as a coulombically trapped bipolarons, although the latter may not exist as free particles. We employ the concept of localized trions in order to explain reversible photoinduced fatigue of thermally stimulated luminescence (TSL) in some poly-phenylenevinylene and polysilylene derivatives. It turns out that the total TSL intensity in these materials decreases after prolonged optical excitations suggesting a slow accumulation of some type of charged states that are more stable than the trapped carriers or long distance metastable geminate electron-hole pairs. Localized trions can be such metastable states. They can be photogenerated via fusion of a photogenerated quasi-free hole and a Coulombically bound pair of an on-chain hole and a deeply trapped electron.

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NON-VOLATILE RE-WRITABLE POLYMER MEMORY DEVICES – A RECENT DEVELOPMENT

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The growth in the usage of organic materials in the fabrication of electronic devices owes to the ease of fabrication of organic electronic devices as well as the applicability of inexpensive substrates in such configurations [1]. Numerous organic materials have been proposed as the basic constituent of devices such as field effect transistors, light emitting diodes and solar cells. However, far fewer attempts have been undertaken to manufacture polymer memory devices [2, 3]. Polymer memory devices are fabricated by depositing a blend (an admixture of organic polymer, small organic molecules and nanoparticles) between two metal electrodes as shown in Fig-1(a). These devices show two electrical conductance states (as shown in Fig-1(b) “1” and “0”) when voltage is applied, thus rendering the structures suitable for data retention. These two states can be viewed as the realisation of non-volatile memory.

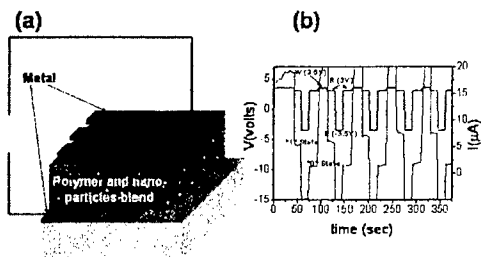


Fig-1(a) Structure of polymer memory devices (b) Current versus voltage response of memory devices during write-read-erase-read voltage cycles

The progress in the polymer memory devices over the last five years will be presented, and invoke the conundrums that scholars of this field are currently faced with, such as questions about the electrical charging mechanism and stability of devices, proposed theories explaining the experimental data, contradictions in the published work by different groups. The proposed answers to the puzzles, wherever applicable, will be presented. The pre-requisites for the realisation of these memory devices will also be presented.

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EXCITON DIFFUSION AND RELAXATION IN LADDER TYPE POLY(PARA-PHENYLENE)

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Excitons in organic materials, including conjugated polymers, play much more significant role than in classical semiconductors. Because of the high exciton binding energy and strong electron localization on individual molecules the charge carrier generation and recombination in organic materials take place via exciton states. Therefore excitons determine many optoelectrical properties of organic materials. Exciton mobility is one of the very important parameters significantly influencing operation of such conjugated polymer-based optoelectrical devices, such as light emitting diodes, or solar cells.

In this report we discuss exciton diffusion properties in methyl substituted ladder type Poly(para-phenylene) (m-LPPP). This polymer is one of the most effective emitters in a blue spectral region and because of its low disorder is very convenient for investigation of general conjugated polymer features.

The investigations were performed by means of ultrafast pump-probe absorption spectroscopy. Three processes, transient absorption depolarization, exciton-exciton annihilation and exciton quenching, were investigated in order to address the exciton diffusion and relaxation rate in different time domains.

Comparative analysis of the transient absorption depolarization in thin polymer films and in polymer solution in toluene shows that the interchain exciton diffusion determines this process already in the subpicosecond time domain indicating a very fast interchain exciton hopping. Similar conclusion comes out from the analysis of the exciton annihilation kinetics. We propose an approach, which enables determination of both the linear relaxation rate and the annihilation coefficient from two exciton relaxation kinetics obtained at different excitation intensity. The annihilation rate coefficient in m-LPPP films remains constant during the entire exciton life-time, which gives a possibility to characterize the exciton diffusion by the time independent diffusion coefficient. The diffusion coefficient, however, changes from sample to sample, evidently depending on the film preparation conditions. The linear relaxation is nonexponential and also dependent on the film preparation.

ELECTRIC-FIELD EFFECT ON ELECTRONIC PROCESSES IN RUBRENE AND TETRACENE

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New tetraphenyl derivatives of tetracene such as rubrene crystal are the subject of the intensive studies during last years opening novel perspectives in the organic electronics [1,2]. According to the recent experiments [2] the rubrene single crystal provides a high field-induced mobility of up to $20 \text{ cm}^2/(\text{V}\cdot\text{s})$ and is considered as a new promising active material for the field effect transistors (FETs) and other nanoelectronic devices. Moreover, the conductivity of the rubrene crystals is high enough to allow STM surface imaging down to the molecular resolution and to observe nearly ideal I - V rectifying p -type behaviour in the point-contact diode devices [3].

Several attempts have been done to understand the nature of the surprising conducting properties of the rubrene. Most of the approaches are based on the semiclassical incoherent hopping model and the assumption that applied field does not change significantly the electronic structure of the molecules, particularly, the shape and localization of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) [4].

We report on the results of theoretical study of the electric field influence on the electronic structure of rubrene and tetracene molecules and crystals. Using quantum chemical calculations performed at the density functional theory (DFT) level we show that the applied field and the side phenyl groups attached to tetracene backbone can play a significant role in the charge transport processes of the rubrene. The calculated evolutions of the HOMOs and LUMOs energy levels and the localization of corresponding wave functions with different applied field strength and direction are compared both for the rubrene and tetracene single molecules. The significant difference in orbital pictures is found between the molecules when field is applied along the side phenyl groups of the rubrene: the growing field magnitude leads to the narrowing of the HOMO – LUMO gap of the rubrene molecule favoring the localization of the electronic density of the LUMO and HOMO wave functions on the side phenyl groups. The conductance mechanisms in rubrene and tetracene crystal structures are discussed.

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PHOTO-ELECTRIC PROPERTIES OF PHTHALOCYANINE FILMS DOPED WITH PARA-CHLORANIL

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Phthalocyanines (Pc) represent an important class of molecular crystals both in fundamental research and in a number of practical applications such as OLEDs, solar cells, OFETs *etc.* Doping of Pc with various organic or inorganic agents is known to change drastically their solid state properties, more particularly conductivity. For instance, co-sublimation with weak or strong molecular acceptors like C₆₀, TCNQ or benzoquinones gives rise to enhancement of light sensitivity or transport characteristics of thin Pc films in multi-layer photovoltaic devices [1].

In many works, the changes in electrical properties upon doping are considered either from viewpoint of intermolecular charge transfer or in framework of the band theory. Alteration of the crystalline state is often neglected or believed to add mainly to the disorder effect in the doped material. In this communication we report on the doping of polycrystalline Pc films by co-sublimation with molecular acceptor *p*-chloranil, CA. Lead phthalocyanine, PbPc (a saucer-like molecule) and metal-free phthalocyanine, H₂Pc (a planar molecule) were chosen as matrix materials. Due to the different architecture, these molecules belong to the different types of Pc crystals. The samples were characterized by AFM, XRD, UV/Vis/NIR and FT-IR spectroscopy and (photo-)electrical measurements.

It has been demonstrated that doping of Pc films by co-sublimation with CA initiates certain regular changes in their crystalline structure, which depend on the type of Pc molecule, but not solely disordering. In itself this factor may inhibit or promote the influence of dopant on the specific conductivity of the particular Pc material, which is associated with formation of stable charge transfer complexes,

CTC [2]. So, the bulk doping of PbPc gave insignificant effect, even in moderately doped films, whereas for H₂Pc the dark specific conductivity increased by 2 to 4 orders of magnitude depending on the dopant content. The overall response of the bulk doped Pc to the white light illumination is usually less than that of intact samples.

In order to elicit the role of interaction with CA on supramolecular level, the surface type cells were fabricated, where acceptor molecules are sequentially sublimed on the ultrathin Pc layer contacting the planar electrodes [3]. By varying the layer thickness, the surface component of conductivity was revealed and assigned to an interface layer entirely controlled by CTC formed over it. The photocurrent action spectra of such two-layer films showed features typical of CTC optical absorption, while both dark and light induced conductivity of underlying Pc layer increased. Taking into account optical transparency and accessibility of CA, it can be proposed as molecular coating for enhancement of spectral sensitivity and specific conductivity of ultrathin Pc layers in photovoltaic devices.

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MICROLASING PROPERTIES OF DYE-LOADED ZEOLITES L

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Zeolite L is a crystalline aluminosilicate that behaves like a nanostructured molecular container forming linear and parallel channels in which luminescent chromophores can be accommodated in the head-to-tail configuration [1]. The

optical "flexibility" of dye-loaded zeolites is quite astonishing. Emission and absorption wavelengths can be independently tuned simply by exploiting energy-transfer processes between two or more types of chromophores, suitably dispersed into the nanochannels. Polarization of the absorbed and emitted light can be selected by using organic dyes with transition dipole lying along the channel direction, or perpendicular to it. In addition, emitter concentration can be changed from a few chromophores per crystal up to densities comparable to those of molecular solids, still showing a very large emission quantum yield.

The aim of this contribution is to take advantage of the favourable optical response of zeolites to realize μ -lasers [2] with controlled emission properties. We present experimental results on the fluorescence characterisation of zeolites L, loaded with three types of molecules: a) *N,N*'-bis(2,6-dimethylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (DXP), b) oxonine (Ox^+), c) methylacridinium (MeAcr^+).

These chromophores have been selected in order to allow for an efficient energy transfer between them, and thus featuring a large absorption/emission Stoke-shift, which should result in reduced optical losses. Due to the difference in length of the dyes, the angle between the transition dipole moment of the molecule and the zeolite L channel axis ranges from 0° for DXP to 72° for oxonine to 90° for N-methylacridine. Zeolite L crystals of cylindric-like shape with $1\mu\text{m}$ -height have been used. Monolayers of different dye-loaded zeolites were deposited on top of a glass or on top of a dielectric mirror, the latter matching the emission wavelength of the lower energy emitter. Zeolites are standing on the substrate surface. Finally, a second dielectric mirror was also gently pressed over the zeolite films to form a vertical microcavity. AFM, confocal microscopy and time-resolved photoluminescence spectroscopy were used to investigate the morphological, optical and lasing properties of the dye-loaded system.

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EMISSION AND RAMAN SPECTROSCOPY OF PHOTOPOLYMERIZED FULLERENE FILMS

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A sustained interest in the study of the photopolymerization phenomenon in C_{60} films is stimulated by the technological applications of polymerized fullerenes as superhard coatings and magnetically ordered materials. Also, polymerized fullerenes are known to exhibit inertness to chemical solvents and possess good mechanical properties which are crucial for enabling fullerene based technologies.

In this presentation the effect of fullerene films photopolymerization on their spectroscopic properties was studied. Fullerene films (thickness 0.5 μm) on the Si substrate were produced by thermal evaporation. The photopolymerized fullerene films were prepared by simultaneous thin film deposition and UV-Visible irradiation method which was reported previously [1]. Photopolymerized C_{60} films were obtained by irradiating the film with a 1000 W Hg lamp during the film deposition in the vacuum chamber. By this method the films with the 50% and 95% polymerization degrees were obtained. Raman spectroscopy was used to evaluate the extent to which the films were polymerized. The intensity of the $A_g(2)$ "pentagonal pinch" mode which appears at 1468 cm^{-1} in the Raman spectra of pristine C_{60} was used as a sensitive indicator for the presence of polymerized fullerene phases in the sample.

In the spectral range 600-1100 nm the luminescence spectra of non-polymerized and polymerized fullerene films were investigated at 300 and 5 K. In comparison with the spectrum at 300 K the spectrum upon 5 K became more structured and new shortwave mode at 695 nm appears, the intensity of which decreases under polymerization. For polymerized films the structured luminescence spectrum was washed off. An approximation of experimental results obtained by the sum of eight separate modes described by Gauss function was performed. The shift of luminescence modes to the red region and the increase of the luminescence intensity after films polymerization were revealed. This phenomenon became significantly apparent in the spectra at 5K. The nature of the emissive centers of fullerene is discussed.

Raman spectra of C_{60} films in the spectral region of the pentagonal pinch $A_g(2)$ and $H_g(7)$ modes ($1380\text{-}1500\text{ cm}^{-1}$) were obtained. The sum of Lorentzian functions was used to fit each Raman spectrum of the fullerene film. At low temperature the bands became narrow. A low temperature study allowed to resolve

two lines 1461 cm^{-1} (chain vibration) and 1466 cm^{-1} (dimer vibration) at 5 K. The intensity of the monomer line (1468 cm^{-1}) increases at low temperature and, on the contrary, the intensity of lines corresponding to the polymeric phase decreases. So, our Raman studies have shown that the photopolymerization degree drops with decreasing temperature. In our opinion, this effect is caused by a phase transition of fullerene that occurred at low temperatures.

Acknowledgments

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PHOTOVOLTAIC EFFECT IN POLYTHIOPENTACENE FILMS AND INFLUENCE ON IT OF CONSTANT ILLUMINATION

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Internal photo-effect in polythiopentacene (PTP) films has been studied by methods of static capacitor and short-circuit current.

Modulated frontal illumination through SnO₂ – electrode and teflon film induces negative charge on a free surface. Spectra of frontal photovoltage (V_f) and absorption of PTP are correlated in 1,40 – 3,45 eV range. Sign of back photovoltage (V_b) is not changed for illumination through opposite SnO₂ – electrode. Its value is smaller by the order comparing V_f . V_b spectrum is anti-correlated with absorption spectrum. Long wavelength band of V_b at 1,48 eV is the same to the analogous band of photoconductivity spectrum [1].

Value of V_f is increased in the region of weak long wavelength absorption under the action of all frontal illuminations. On the contrary strongly absorbed illumination at 1,73 and 2,67 eV and weakly absorbed illumination at 2,15 eV change V_f sign. In the region of strong long wavelength absorption of PTP strongly absorbed illumination at 1,73 and 2,67 eV decreases, and weakly absorbed illumination at 1,51 eV increases V_f value. All back illuminations change the sign of V_b in spectral range 1,4 – 2,0 eV.

Spectrum of short-circuit photocurrent under illumination via Ag electrode for Ag/PTP/Al sandwich structure is close to V_b for capacitor-cells, and under illumination via Al is close to V_f .

The experimental results obtained evidence that of PTP films have hole conductivity. V_f is the sum of oppositely directed bulk Dember photovoltage and surface barrier photovoltage, caused by anti-blocking band slope near free surface of PTP. Main deposit in V_b gives surface barrier photovoltage due to anti-blocking band slope near back electrode. Band slope near Ag- and Al-electrodes are anti-blocking and blocking, respectively.

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INVESTIGATION OF ENERGY MIGRATION ON TRIPLET LEVELS IN THIN FILMS OF ORGANIC MOLECULES

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Tripлет energy transfer was investigated in the multilayer films. Anthracene was energy donor. The dye Rhodamine C was energy acceptor. Anthracene films were obtained on quartz substrate by vacuum deposition. Dye film was deposited by Langmuir-Blodgett (LB) method on the surface of the anthracene film. The number of the monolayers was 20. Excitation was performed by nitrogen laser pulses in the donor absorption band. The registration of the delayed luminescence signal was carried out in 50 μ s from the beginning of the excitation. The measurements were performed at sample temperature $T=90$ K. While exciting in the anthracene absorption band, the bands of annihilation delayed fluorescence of the anthracene monomers ($\lambda_{\text{max}}=500$ nm) and excimers ($\lambda_{\text{max}}=500$ nm) were observed. Besides, the band of long-lived luminescence the maximum of which had the wavelength of 595 nm was observed. The spectrum of this band coincided with fluorescence spectrum of LB films at excitation in the dye absorption band. Increasing dye concentration in a monolayer led to quenching of anthracene luminescence and growth of the long-wave luminescence band intensity. Kinetics of the anthracene and rhodamine luminescence decay has complicated form. The initial part of the kinetics curves is described by power function and long-lived part by exponential function. Luminescence duration calculated by exponential part changes from $\tau=2.04$ ms to $\tau=0.86$ ms when rhodamine concentration (C)

changes from 0 to 75 mol%. The lifetime of sensibiliized acceptor luminescence also depends on dye concentration and amounts to $\tau=1.82$ ms for $C=50$ mol% and $\tau=0.68$ ms for $C=75$ mol%. At photoexcitation of the film in the donor layer triplet excitons will be formed. Migrating exciton having reached the film surface can collide with dye molecule built into LB film structure. As a result of reaction of triplet-triplet energy transfer, acceptor triplet molecules will be formed in LB films. A molecule of rhodamine C has low quantum yield of the intramolecular triplet singlet transfers. So that one should suppose that luminescence observed is a result of the annihilation of the dye triplet excitations in LB film. The intensity of the sensibiliized luminescence decreases in magnetic field. The maximum value of magnetic effect is 11.3%. Temperature influence on the efficiency of triplet exciton migration was investigated. Analogous investigations were performed for the system "anthracene - Nile red". At excitation in the absorption band of energy donor the sensibiliized luminescence with the maximum at wavelength of 640 nm was observed. The duration of donor molecule luminescence in the heterofilm decreased to $\tau=1.4$ ms for dye concentration in LB films of 50 mol%. The lifetime of sensibiliized acceptor luminescence is 2.4 ms for $C=50$ mol%.

PHOTOPHYSICAL PROPERTIES OF CATION CYANINE DYES IN SOLUTIONS AND LANGMUIR-BLODGETT FILMS

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In the work the spectral and luminescent properties of a surface-active cation oxacarbocyanine dye in different solutions and Langmuir-Blodgett (LB) films have been investigated.

It was established that dye absorption and fluorescence spectra in ethanol, chloroform, and polyvinylbutyral practically have the same shape. Maximums of the spectra are a little shifted with respect to one another because of different solutions polarity. The oscillator strengths of the electron transitions and quantum yields of the dye fluorescence in solutions were determined. It was found that dye molecules in solutions were in monomer form. The delayed fluorescence of the dye in polyvinylbutyral was revealed.

Monolayers were formed at the water-air interface on a Langmuir trough. The pure dye monolayer and the mixed monolayers of the dye and stearic acid

with molar ratios of 50:50, 25:75, 17:83, 9:91 mol% respectively were investigated. Monolayers were transferred onto quartz substrates by vertical dipping according to Z-type transfer (transfer during upward stroke) at surface pressures of 30 mN/m.

The surface pressure-area isotherms of the dye monolayers were measured. It was found that isotherm of the pure dye monolayer is typical to liquid-expanded state. When compressing mixed monolayers, the transition from liquid-expanded state to condensed state takes place. From the isotherms the surface areas of the dye molecule at different monolayer phase states were determined. Obtained data and results of conformational analysis of the dye molecule, performed by method of molecular mechanics in the force field MM+, point that in the pure monolayer the chromophore plain of the cyanine molecule lies on the surface of water subphase, and in the mixed monolayers the chromophore plain is oriented perpendicular to subphase surface.

Electron absorption spectra of the dye LB films consist of two bands. The ratio between the band intensities depends on the dye concentration. With concentration increasing the intensity of the short-wave maximum increases, and the intensity of the long-wave one decreases. At that, all the spectral curves cross at an isobestic point, which points to presence of two types of absorption centers: monomers and dimers. Long-wave band corresponds to monomers and short-wave one to dimers. Fluorescence spectra of LB films essentially differ from dye spectra in solutions.

Quantum-chemical calculations of electron structure of the dye molecule in approximation of Pariser-Parr-Pople method taking into account configuration interaction were carried out.

SPECTROSCOPIC PROPERTIES AND PROCESSES OF PHOTODISSOCIATION OF DYES

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Use of dyes as environments for generation of the laser radiation produces increased requirements to the physical and photochemical properties of molecules of dyes. In particular, they should have the high quantum output of fluorescence in the required spectral region and to be steady against action of exciting light and laser radiation. At the same time it is clear, that all molecular compounds without exception photodissociate at the light irradiation in that range of the wave lengths,

which corresponds to the localization of the excitation on one of the loosening σ^* -bonds. The excitation of dye in the laser environment can be carried out with the help of multiquantum processes, with which it is necessary to learn to struggle.

The present report is devoted to the description of the experimental (the spectroscopic and photochemical investigations) and theoretical (the quantum-chemical calculations and the calculation of the kinetics of the physical and photochemical processes) researches of the behaviour of dyes depending on the wave length of the exciting light at influence of the excitation of the various intensity. In particular, the properties of one of the representatives of the oxazine dyes – resazurin are studied.

The characteristic feature of the molecule structure of resazurin is the presence of the N-O bond of the donor-acceptor type which has appeared owing to interaction of the completely occupied $n(sp^2)$ molecular orbital (MO) of nitrogen and the unoccupied p-MO of the exited oxygen atom.

The solution of resazurin in acetone is characterized by the absorption spectrum containing the long-wave band at $\lambda = 630$ nm. The corresponding luminescence band of resazurin lies at $\lambda = 650$ nm and it has the high quantum output. At replacement of the solvent (ethanol, water etc.) the absorption band is widened and displaced to the short-wave side, and the quantum output of fluorescence is decreased. The reactions of the acid-base balance are characteristic for the resazurin molecule, owing to what at addition of the acid in the solution the protonation of the molecule occurs, and at addition of alkali the deprotonation with formation of the symmetric structure take place in both cases.

The investigation of the photochemical processes has allowed to show, that the irradiation of the solution of resazurin with UV light results in localization of excitation on the dissociating N-O-bond and, as a consequence, to the one-quantum processes of dissociation of the molecule with break of the donor-acceptor N-O-bond. At that the resorufin molecules, having negligible fluorescence are formed.

At the light irradiation from the visible spectrum the two-quantum processes of decolouration of dye with formation the same resorufin is observed. This process includes the singlet-singlet excitation, singlet-triplet conversion and triplet-triplet excitation. Thus, the high-excited triplet state of the molecule is reached.

The investigation of the line of dyes has shown that the one-quantum and two-quantum processes result in the identical photochemical processes of decolouration of dye not always, if the reactions of phototransfer of an electron between the dye molecule and solvent are included in the process.

THE ELECTRONIC STRUCTURE AND POLYMERIZATION OF A SELF-ASSEMBLED MONOLAYER

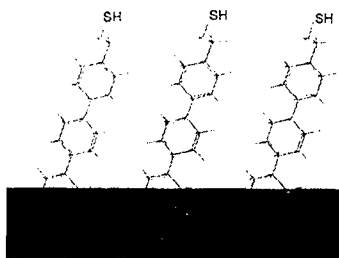
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Although organic adsorbates and thin films are generally regarded as “soft” materials, the effective Debye temperature, indicative of the dynamic motion of the lattice normal to the surface, can be very high, e.g., in the multilayer film formed from [1,1'-biphenyl]-4,4'-dimethanethiol (BPDMT) [1]. The effective Debye temperature, determined from core level photoemission from the all carbon arene rings, is comparable to that of graphite, and follows the expected Debye-Waller behavior for the core level photoemission intensities with temperature, but this is not always the case. (We associate this rigidity to the stiffness of the benzene rings, and the ordering in the ultrathin multilayer molecular thin film.)



We find that a monomolecular film formed from [1, 1';4',1'']-terphenyl]-4,4''-dimethanethiol deviates from Debye-Waller temperature behavior and is likely caused by temperature dependent changes in molecular orientation [2].

Intermolecular π - π lateral interactions for [1, 1';4',1'']-terphenyl]-4,4''-dimethanethiol (TPDMT), were evident from the considerable dispersion of the TPDMT molecular orbitals with changing the wave vector k . The highest occupied molecular orbitals hybridize to electronic bands, with a band dispersion of about 300 to 400 meV. The wave vector dependence is consistent with a lateral spacing of about 5.1 Å, found in STM.

We also find evidence for the increase in dielectric character with cross-linking in spite of the decrease in the HOMO-LUMO gap upon irradiation of TPDMT. The cross-linking processes are also accompanied by changes in molecular orientation.

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VIBRATIONAL AND ELECTRONIC PROPERTIES OF PHTHALOCYANINES FILMS WITH FULLERENES C₆₀

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The derivative of porphyrin, which involve also phthalocyanines, plays significance part in the transfer of excitons and electrons in the molecular biosystems. Phthalocyanines can to create the stable complexes of ligand with the metal atoms due to the formation of symmetric donor-acceptor bonds. At this the most expressed donor-acceptor bonds are observed for complexes with the ions of transitional metals possessing large affinity to the electron. It is interest to consider the complexes of crystalline phthalocyanines with fullerenes, which are effective electronic acceptors. Obviously that formation of such complexes can to affect substantially on inside donor-acceptor interaction of phthalocyanine that must to exhibit in the change of vibrational spectra of these systems.

The study of Raman and IR (infrared) spectra, and crystalline structure of phthalocyanine films with a different fullerene C₆₀ contents is the purpose of the given work. Phthalocyanine films without metal and with the metal atoms with fullerenes C₆₀ have been obtained by vacuum condensation on undercoat at simultaneous sublimation of both types molecules from different thermal sources. The thick of films is about 100 nm. The contents of the fullerenes are changed from 0,1 to 5 gravimetric percents of C₆₀.

Noted that aggregation of fullerenes with the origin of their crystalline phase at the high concentrations of C₆₀ is observed. At small C₆₀ concentrations β -modification of monocline crystalline structure of phthalocyanine, the parameters of which change as fullerene contents increases have been observed. This indicates on embedding substitution of the admixture element. Raman and IR spectra bands for phthalocyanines is conserved, however they undergo splitting and displacement, which change not monotonically in region of the low C₆₀ concentrations. Similar changes take place in the spectrum of vibrational modes of fullerenes. The obtained results are explained of formation of complexes of phthalocyanine-fullerene by the origin of donor-acceptor interaction, which changes depending on contents of the C₆₀ molecules and presence of metals in phthalocyanine, that is appeared in electronic transfer spectra at measurements of optical conductivity.

INFLUENCE OF SUBSTRATE TEMPERATURE ON EFFICIENCY OF CARRIER PHOTOGENERATION AND EXCITON DIFFUSION IN VACUUM DEPOSITED FILMS OF A PERYLENE DERIVATIVE

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The morphology, optical and photovoltaic properties of N,N'-dimethylperylene-tetracarboxylic acid diimide (MPP – methyl perylene pigment) films were investigated in the present work. MPP films were thermally deposited at various substrate temperatures (Ts). The morphology of the films was measured with a "Nanoscope IIIa" Atomic Force Microscope (AFM). Optical spectra (absorption and luminescence) were measured with "Hitachi" spectrophotometers. Photovoltaic properties of MPP films were investigated by the Bergman technique.

All prepared films were polycrystalline. The shape and size of the crystallites essentially depends on Ts. At Ts = 300 K the crystallites have oval (smoothed cone) shape, 40-70 nm in size and are preferentially oriented perpendicular to substrate. And at Ts ≥ 370 K ribbon-shaped crystallites dominate in the films. The ribbon-shaped crystallites are 100-200 nm wide, their length reaching 1000 nm as Ts increases. The transition between the two forms of crystallites begins at Ts ≈ 330 K. The shape and size of crystallites weakly depends on the type of used substrates. It should be noted that the roughness of the films deposited on ITO is lower than that on quartz.

Increasing of Ts from 300 K to 370 K results in an increase of the photovoltage and photosensitivity of MPP films. The highest photovoltage and efficiencies of photogeneration of charge carriers in MPP films was observed at Ts ≈ 370 K. The photosensitivity increase is caused both by an increase of diffusion length of excitons and by a decrease of the surface recombination rate. The diffusion lengths of Frenkel excitons were estimated to increase from 25 to 55 nm for Ts rising from 300 K to 350 K. Simultaneously, the diffusion lengths of charge transfer states increase from 10 to 25 nm.

The recombination rate of both Frenkel excitons and charge transfer states is higher on the free surface than at the ITO/MPP interface, irrespective of Ts. This can be caused by a preferential adsorption of molecules of air (for example, oxygen) on free surfaces of MPP films, resulting in a high concentration of recombination centers for charge carriers.

The results of the investigation of the morphology, and optical and

photovoltaic properties were analyzed assuming the existence of dimeric aggregates in vacuum deposited MPP. The obtained results can be rationalized assuming the presence of two types of dimeric aggregates.

These results can be used for improvement of parameters of organic solar cells based on MPP.

The research reported in this contribution was supported by the Ministry of Education and Science of Ukraine and of Education and Science of Poland within the Polish-Ukrainian collaboration grants.

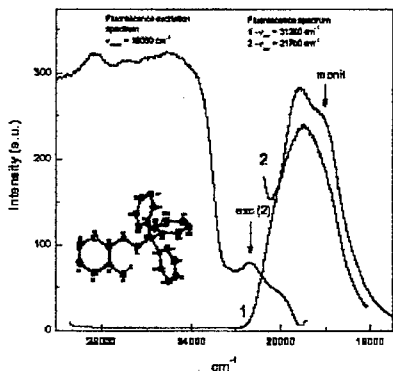
THERMALLY MODIFIED AND PHOTO-INDUCED PROTON TRANSFER PROCESS OF *N*-TRIPHENYLMETHYLSALICYLIDENEIMINE

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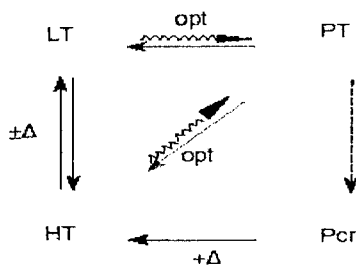
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N-triphenylmethylsalicylideneimine (MS1) represents a reversible solid-state photocoloration system. The photochromic unstable form is created after an excited-state proton transfer reaction at low temperature, only. We have postulated that the photocolored (orange) species, created below 240 K, is a trans-keto isomer, and the open trans-enol excited form existing in ground state is a source of that orange species. The barrier of the fading reaction cannot be interpreted as a simple thermal keto-enol isomerization.



Luminescence spectra of MS1:

1 - fluorescence of the PT form, 2 - fluorescence of the Pcr form and (on the left) fluorescence excitation spectra of crystalline sample at 77 K; photochromic absorption band ($\lambda_{max} = 21700 \text{ cm}^{-1}$) and energy of monitoring the emission spectrum are pointed out by arrows.



Scheme (simplified): the main steps of the molecular rearrangement of MS1 - in a solid state; LT (white), HT (yellow), PT, Pcr (orange) – low- and high-temperature, proton-transferred and photochromic forms of MS1, respectively; Re – rearrangement in excited state, opt - optical transitions (absorption, fluorescence), $\pm \Delta$ - thermal processes.

Using DSC technique on a non-irradiated sample, pseudo-first order phase transition at 241 K was identified with the enthalpy equal to $H = 0.35$ J/g. The initial stage of the system studied before the photoreaction was defined by means of X-ray structure analysis. Taking into account the results of the differential scanning calorimetry measurements, crystal structures were done at 295 and 230 K. Temperature resulted changes in geometry are focused mainly on angular relationships in a chelate six-membered ring. The molecular librations hindered at low temperature brought about irregular changes in single and double bond lengths of all phenyl rings. The experimental activation energy equal to 24.7 and 39.7 kJ/mol, have been obtained from thermally driven changes in luminescence spectra.

EFFECT OF SUBSTITUENTS ON PHOTO- PROPERTIES OF DECAHYDROACRIDINE DERIVATIVES WITH REGULAR STRUCTURAL CHANGES

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One of the problems of molecular photoelectronic is goal-directed creation of materials with properties set in advance. To influence on properties of photosensitive materials it is possible by the change of characteristics of environment or modification of the structure of photosensitive component. The association between the structure of molecule and photo- properties of a substance

on the example of 3,3,6,6-tetramethyl-N-phenyl-decahydroacridine-1,8-dione derivatives with regular change of molecular structure is investigated in this paper. The initial molecule of the basic compound was modified by the introduction of substituents with different donor-acceptor properties.

The researches shown that the spectra of an electronic absorption and photoluminescence of compounds practically are not depend on the position and properties of the introduced substituents. Ethanol solutions of all substances have the similar spectra of absorption in the region of $\lambda \approx 200-400$ nm with the maximum of long-wave band with $\lambda_{\max} = 375 - 390$ nm. The spectra of luminescence of all compounds have a single unstructured band with $\lambda_{\max} \sim 455$ nm. Practically constant position of absorption and luminescence bands even at introducing substitutes with the relatively extensive π -electron system, namely $R_2 = \text{COO-C}_4\text{H}_9$, testifies to absence of a conjugation between the decahydroacridine fragment of molecules and substituents.

Unlike spectral properties of dyes their photochemical properties strongly depend on the substituents. The basic compound is photosensitive. Under action of UV-irradiation there is phototransformation of molecules, which is accompanied by coloring of compound in a red color, appearance in the spectra of absorption of a new band with $\lambda_{\max} = 500$ nm and luminescence quenching. At introducing of the electron-donor CH_3 substituent the change of photochemistry properties of substance is observed. It becomes photostable and does not change the spectral characteristics under action of UV-irradiation. Photostability of derivatives of decahydroacridine increases at presence of substitute in p-position with electron-donor properties (Cl, OH). However, at the change of properties of substituent in p-position with electron-donor on electron-acceptor ($\text{COO-C}_4\text{H}_9$), the substance becomes photosensitive again and UV-irradiation results in the increasing of intensity of absorption band in the visible range of spectra.

The essential difference in efficiency of photochemical transformation processes in dyes at UV-irradiation caused by various donor-acceptor properties of the entered substituents are revealed. The mechanism of phototransformations has been proposed which is in the accordance both with the electronic structure of molecules and the spectral characteristics of the initial and irradiated substances. The analysis of calculations of electronic density distribution in molecules with different substituents and experimentally observed changes of spectra under the irradiation of compounds allows defining the scheme of molecules phototransformation and mechanism of substituents influence on efficiency of phototransformation. It is stated that at UV-irradiation of dyes solutions there is an oxidation of the photoexcited molecule with formation of pyridine ring in an ethanol, and it is explained the influence of substitutes on efficiency of process by the change of distribution of electronic density in a molecule.

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EXCITED STATE DYNAMICS OF INDANDIONE CLASS COMPOUNDS

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Indandione class molecular materials have been demonstrated to have large optical nonlinearities and significant photoelectrical sensitivity [1]. Large dipole moment of this class of molecules and its significant change under excitation make them interesting for prospective applications in various electrooptical devices. Due to their structural flexibility and strong molecular-environment interaction these compounds exhibit very different optical properties in liquid solutions, dispersed in polymers and in solid state [2].

Here we report investigation results of the new indandione based compounds. Steady-state and ultrafast pump-probe absorption spectroscopy methods were applied to investigation of the absorption, fluorescence and excited state dynamics of the indandione compounds in solutions and in solid state. Excited state dynamics and fluorescence properties were found to be strongly affected by the molecular conformational relaxation in the excited state. Excited state twisting of the molecules over different flexible bonds leads to formation of nonradiative states and subsequent ultrafast excited state deactivation or to creation of radiative conformers. These processes are determined by the structure of substituents connected to the indandione fragment and by the solvent viscosity. In polymeric matrix the molecules have less freedom for conformational motions, therefore their excited state dynamics is less affected by the conformational motions.

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PHOTOPHYSICAL PROCESSES IN SOME IMINOCOUMARINE DERIVATIVES

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Coumarins are an extensive class of the compounds having both artificial, and a natural origin. Many aminocoumarins have been found wide application as active media in dye lasers for a blue-green range. The some coumarins of a natural origin are biologically active substances and are applied for preventive prophylaxis and treatment of thromboses, and also for other purposes. Properties of iminocoumarins have been studied poorly.

In this paper experimental researches of the spectral-luminescent properties of 3-pyridyl-7-hydroxy-2-iminocoumarine and 3-(2-methylthiazolyl)-7-hydroxy-2-iminocoumarine have been investigated in ethanol solution at various pH values and in other solvents of the different chemical nature and polarity. Spectral properties of ionic forms of these compounds were studied with quantum-chemical method INDO/S with spectroscopic parametrization [1] also. By means this method, rate constants of internal and intersystem conversion and protonacceptor properties were estimated. The lasing properties of these molecules were investigated at excitation with excimer XeCl – laser.

It was shown that in the longwave area of a spectrum (300-500 nm) the compounds have two absorption bands, and shorter wavelength band belongs to the neutral form (NF) of molecules, and the second - to a zwitterion (Z) formed by simultaneous proton breakaway from OH-group and protonating one of the nitrogen atoms. In acidulous solutions, at HCl concentration $\sim 10^{-1}$ M, both compounds exist in the cation form. In alkaline solution ($C_{NaOH} \sim 10^{-3}$ M) an ion-neutral balance moves to anion forms formations. All protolytic forms exhibit bright fluorescence but NF possesses the highest fluorescence quantum yield. In ethanol NF and Z emit simultaneously.

Researches in various polarity solvents have shown that these compounds exhibit weak solvatochromic properties.

The spectral data of quantum –chemical investigations of all protolytic forms of the coumarins are in a good correlations with experimental ones. It was shown that molecule structures are non planar, the substitute in 3-th position is out from coumarins skeleton

To determine the center of protoning in the molecules the method of molecular electrostatic potential (MMEP) was used. On MMEP maps there are two deep minimums which are caused with nondivided electron pairs on the nitrogen atoms of iminogroup and substitute in 3-th position. It was shown, that an energy minimum near from iminogroup nitrogen is deeper, than at nitrogen of

substitute. On the basis of this data we have concluded that a first protoning in molecules is more possible on iminogroup nitrogen.

Investigation of laser properties in ethanol solutions has shown that both compounds exhibit non effective lasing, and the laser spectra lies in the fluorescence band of Z. The quantum -chemical calculation of triplet-triplet absorption has shown, that in the field of NF fluorescence there are no strong T-T absorption that could be the reason of NF lasing absent. The absence of lasing of NF is caused with reabsorption of NF radiations with Z molecules, the spectra absorption of that superimpose on NF fluorescence. The observed lasing thus belongs to zwitterions of studied compounds.

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CURRENT-VOLTAGE CHARACTERISTICS OF A TWO-SITE MOLECULE WITH A WEAK INTER-SITE COUPLING

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To clarify the role of localized molecular orbitals in formation of an electron current through a single molecule embedded in between the microelectrodes we have considered a model of a two-site molecule with a weak inter-site coupling. The objective is to obtain the exact analytic expressions for the current and the conductance. It is supposed that both centers of electron localization within the molecule are close to respective electrode surfaces and thus can be treated as the terminal groups of the molecule. At such position of the sites, there is no a pronounced dependence of electrode-molecule couplings on an external electric field. It means that a dependence of molecule conductance on the applied voltage is governed by the shifts of molecular electronic levels in an electric field. The shifts depend strongly on the position of the sites with respect to the electrodes. We show that a level localization leads to asymmetry in the current-voltage and conductance-voltage characteristics of the molecule not only owing the asymmetric position of the molecular sites relative to the electrodes but also the dependence of the intersite coupling on the applied voltage. If the shift of localized molecular levels is asymmetric then a resonant transmission through each molecular level occurs at different resonant voltages. It leads to a different absolute value of resonant voltages at positive and negative direction of the applied electric field. We also show that if the intersite coupling becomes

comparable with the couplings of the terminal molecular sites to the electrodes, the current formation is defined by a complicated mixture of elastic and inelastic (hopping) transfer processes in the device "electrode-molecule-electrode" [1,2,3].

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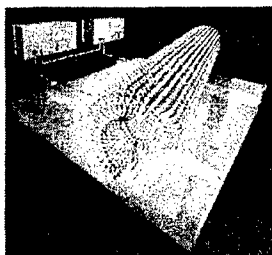
PHOTOELECTRONICS OF COMPOSITES BASED ON ORGANIC CARBON NANOTUBES

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Functional materials with nanometric precision have attracted great attention. We have developed a variety of such functional materials based on inorganic frameworks, organic self-assembly, and biological macromolecules. Examples include dendritic macromolecules for light-harvesting, light-emitting, imaging, and magnetic materials, mesoporous silicates for polymer processing and unidirectional alignment of functional organic molecules, discrete inorganic rings containing functional organic modules, oligopeptide-based helical spaces for stereochemical recognition of helices, tubular protein assemblies for stimuli-responsive nano containers, soft polymeric materials with carbon nanotubes, metalloporphyrin-based nanospaces for trapping fullerenes, and self-assembled graphitic nanotubes.

Some of those materials show very unique properties. In particular, we recently found that bucky gels, prepared by grinding single-walled carbon nanotubes in imidazolium ion-based ionic liquids (1, 2), serve as highly powerful capacitors, and can be applicable to the fabrication of fully plastic actuators by layer-by-layer casting (3). Graphitic nanotubes, prepared by self-assembly of an



amphiphilic hexa-*peri*-hexabenzocoronene, are also interesting electronically active materials (4). We recently succeeded in obtaining a pseudo-crosslinked version of this graphitic nanotube by ADMET-triggered self-assembly of an allyl group-appended new amphiphilic hexa-*peri*-hexabenzocoronene (5). We have also developed photo and redox-mediated covalent stabilization of the graphitic nanotubes (6, 7). Use of a chiral amphiphilic hexa-*peri*-hexabenzocoronene with stereogenic centers results in the formation of graphitic nanotubes with one-handed helical chirality (8, 9).

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HOMO- AND HETEROEPITAXIAL SELF-ORGANIZED MOLECULAR ARCHITECTURES: STM STUDY AT THE LIQUID-SOLID INTERFACE

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Self-organized architectures of organic molecules on atomically flat surfaces have attracted great interest in view of theoretical aspects and potential applications. Since the discovery of scanning tunneling microscopy (STM) this method has been a unique tool for the investigations of such systems with molecular resolution in ultra high vacuum. An alternative to vacuum deposition in the preparation of well-defined molecular architectures is based on self-assembly of molecules at the *liquid-solid interface* under ambient conditions. We present the systematic STM study of different self-assembled nanostructures at the liquid/Au(111) and liquid/graphite interfaces [1-3]. Investigated molecules: long *n*-alkanes, C_nH_{2n+2} ; discotic liquid crystals (triphenylenes, hexabenzocoronenes, triazatraphylenes); trimethylsilyl-acetylene derivatives (as alternative to thiole SAM's); fullerenes, C_{60} , C_{70} and their derivatives.

We also show that graphite surfaces modified by organic templates such as

long *n*-alkanes and benzocoronenes can serve as new substrates for formation of new highly organized systems [4]. The results of observations of phase transitions, single-molecule and single-nanocluster manipulations are presented. The observed structures are discussed in terms of commensurability and interfacial interactions.

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ELECTRONIC PROCESSES IN CONDUCTING POLYMER - SEMICONDUCTOR INTERFACE

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Heterostructures based on organic and inorganic semiconductors excite a grate interest for development of the different type sensors, solar sells and electrooptic devices. We have investigate a systems based on heterojunction of conjugated polymers and inorganic semiconductors with layered crystal structure of A^{III}B^{VI} type (InSe, GaSe), porous silicon (PS) and transparent ITO electrodes to study their potential using in sensor devices, solar cells and electrochromic displays.

As polymer materials suitable to photo-power generation in heterostructures with A^{III}B^{VI} semiconductors the poly-phenylacetylene (PPA) and polyaniline (PANI) are studied. It has been shown [1,2] that using of conducting polymers in heterojunction with InSe give a possibility to widening of the spectral range of photosensitivity. In solar cells based on dispersed InSe- polyaniline composites the current – voltage characteristics in the dark could be modelled by using Shockley equation [3].

To obtaining the integrated polymer-porous silicon nanostructures a method of electrochemical polymerization of aniline and *o*-methoxyaniline on the surface both *n*- (100) and *p*-type (111) PS has been used [4]. The layers of PPA were

deposited from solution in organic solvents, poly-para-phenylene (PPP) was deposited by vacuum evaporation. Obtained structures were studied by FT-IR spectroscopy, X-ray analysis, atom force microscopy and examined on the ability to photo- and cathode luminescence. A significant effect of polymer nature and thickness on current-voltage characteristics, luminescence and photosensitivity of PS-CP and CP-ITO heterojunctions may be a ground to gas and pH sensors development.

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MECHANISMS OF CONDUCTIVITY IN METAL-POLYMER-SI THIN FILM STRUCTURES

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Since the discovery of conducting polyacetylene, the number of scientific publications devoted to study of thin films based on different polymers grows from year to year. Manufacture of various multilayer film structures based on silicon and polymers [1] and investigation of electrical properties of polymers and mechanisms of charge transfer in them remains as an actual problem.

In this connection by the purpose of the present work was the experimental study of conductivity mechanisms in thin polymer films, which are included in heterostructures based on silicon. As the basic technique of measurements the current-voltage characteristic method was chosen in the temperature interval 300-80K. Thin polymer films were prepared by spin coating of a polymer solution on p-Si wafer. The upper electrode was applied on the polymer film by vacuum evaporation. As a polymer a thin film of polydifenylphenylene is used, in which the transition from dielectric to a high-conductivity state was earlier observed [2].

The conductance of the polymer film ($\ln(I/U)$ vs. inverse temperature ($1000/T$)) is explored. The dependences of a current on inverse temperature carry exponential character with different energies of activation on various sites. The analysis of curves allows us to assume, that this or that charge transport mechanism predominates depending on quantity of an applied electric field and temperature interval.

Apparently, at high temperatures the current connected to Schottky thermionic emission acts. For confirmation of this assumption the dependences $\ln(I/T^2)$ vs. $1000/T$ were constructed. In conductance of films in low temperature interval the contribution of electrons with energy near to the Fermi level is apparently appreciable, and electrons jump between the localized states. In this case dependence of an electrical conductivity on temperature looks like: $\sigma \sim \exp(-w/kT)$, where w is the activation energy of a jump.

Besides its temperature dependence, the hopping transport is also characterized by electrical field dependence of conductivity. To find out features of charge transport the dependences of the films conductance $\ln(I/U)$ vs. $U^{1/2}$, i.e. in the Poole-Frenkel coordinates, are also constructed. The experimentally found values β differ from β_{PF} within the framework of the Poole-Frenkel model. For explanation of these distinctions we have involved a hopping model with a Gaussian distribution of localized levels [3], according to which $\ln \mu \sim F^{1/2}$.

Thus the experiments in the given work, allow us to make preliminary conclusions about the basic mechanisms of charge transport in different electric field and temperature intervals. In our samples the charge carriers transport, most likely, is explained by Schottky thermionic emission and hopping mechanisms.

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GOLD-LIQUID ELECTROCHEMICAL INTERFACE-PECULIARITIES FOR OPTOELECTRONIC DEVICES

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Recently developed electrochemical surface plasmon resonance (ESPR) technique attracts the scientific attention due to possibility to perform the optical and electrical measurements of surface processes simultaneously [1]. The surface of evaporated gold films widely used in sensoric of nanofilms as sensitive element that allows the chemical modification. The gold film as work electrode in electrochemical sensors can be used also. For the cases, when surface of gold is covered by electrolyte solution, at the interface metal-liquid starts the electrochemical processes, which influence on the physical-chemical properties of sensor, especially if electric field there exists. In the attenuated total reflection (ATR) configuration an evanescent wave generate the surface plasmon-polariton (SPP) that results in strong enhancement of electric field at the interface gold-ambient. Accordingly, electrochemical processes at the metal surface even without application of external electric potential have place. In presented work the behaviour of angle position of SPP (SPR response) as well as effect of enhancement of infrared (IR) absorption by rough metallic surface (SEIRA) at the interface gold-liquids was studied. It is important due to noticed factor of instability of SPR response, which influence on the results of measurements and sometimes make impossible the interpretation of SPR results. As was founded, the main contribution in the instability of SPR angle position and SEIRA effect yields the roughness of surface of evaporated gold that usually is estimated on the range about of 3-5 nm and can be little decreased by thermal annealing. The SPR and SEIRA measurements was performed for uncovered surface of gold film after initiation of electrochemical processes by short time immersion into the different solvents, which expose polar and non polar properties. Surface roughness of metal could increase adsorption of gazes or ions from liquid at a gold surface. In our case we observe the increasing adsorption of N₂ on gold substrates of different roughness and changing of electric potential at the interface gold-liquid as well. Supported Au catalysts can oxidize molecules such as CO at, or even below, room temperature. This is all the more surprising because flat Au by themselves is not particularly active for CO or O₂ adsorption [2].

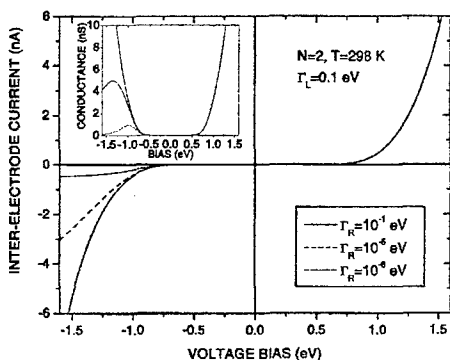
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CURRENT ASSYMETRY CAUSED BY MOLECULAR-ELECTRODE CONTACTS

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A theoretical model of formation of the combined elastic and inelastic interelectrode current through a regular molecular wire embedded in between the electrodes is applied to study the influence of molecular-electrode contacts on rectification properties of a molecular wire. It is assumed that the LUMO-levels related to the internal wire units are energetically positioned much higher the electrode's Fermi-levels as well as the levels belonging the terminal units. In this case, the terminal units act as the intermediate donor and acceptor centers with respect to the interior wire units controlling thus a current formation via distant superexchange and thermally activated sequential pathways [1]. The current and the conductance of a molecular wire is evaluated in the condition of a weak electron-vibrational coupling. Two limited cases of strong and weak coupling of terminal wire units to the electrodes are analyzed. Analytic expression for an important case of the molecular wire with two interior units is derived. It is shown that in the case of strong electrode-terminal unit couplings the current formation is associated with two alternative (superexchange and sequential) mechanisms. But, in the case of large energy gap between the terminal and interior wire units a role of sequential mechanism becomes minor. Therefore, the current is mainly determined by an elastic mechanism. At weak molecule-electrode couplings both elastic and inelastic transfer processes become responsible for a current formation.



The figure illustrates the appearance of asymmetric current-voltage characteristics of a molecular wire caused by the molecule-electrode couplings. A pronounced rectification effect appears at strong difference between the couplings (through the width parameters Γ_L and Γ_R).

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ANISO-TYPE HETEROSTRUCTURES BASED ON MPP

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Aniso-type heterostructures (HS) based on organic semiconductors are actively used for the development of organic solar cells and light-emitting diodes [1-3]. But at present time the photo-conversion efficiency for these HS isn't sufficient for practical application. One of the important reasons of this low photo-conversion efficiency is the absence of the criteria for selection of optimum components for the creation of effective organic aniso-type HS and these criteria should be associated with the parameters of energy structure.

Therefore, the aim of this work was the study of organic aniso-type HS with different parameters of the energy structure of the p-type components. In contrast to inorganic semiconductors, the majority of photosensitive organic semiconductors weakly absorbs sunlight in the range 400-550 nm that leads to low photo-conversion efficiency under AM 2 illumination. To decrease this negative property we have used films of N, N'-dimethyl perylene-tetracarboxylic acid diimide (methyl perylene pigment – MPP). MPP is one of the most photosensitive organic n-type semiconductors and effectively absorbs light in the range 400-550 nm. Since the effect of substrate and annealing temperature on properties of these films is weakly investigated, we carried out special studies of substrate and annealing temperature influence on optical and photovoltaic properties of MPP films. It was established that the maximal photosensitivity is reached at 370 K substrate temperature, and the influence of annealing is less effective than effect of substrate temperature.

The films of organic semiconductors with different band gap and work function were used as p-type components. All HS were thermally deposited in the vacuum on substrate with conductive ITO layer. Photovoltaic properties of HS were investigated by Bergman technique under the modulated illumination of the different sides of HS. This technique allows to check the presence of barriers at the bottom ITO-electrode of HS and at top free surface.

We compare obtained results with the parameters of energy structure of aniso-type HS, according to Anderson's model without taking into account surface states. The reasons of deviation of the obtained results from Anderson's model are analyzed.

The maximal photosensitivity was achieved for MPP/pentacene HS prepared at substrate temperature 370 K. However, MPP/lead phthalocyanine HS at optimization of technological conditions may be also well promising, as these HS effectively absorb sunlight in the wider spectral region than MPP/pentacene HS.

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EFFECT of AIR on PHOTOPHYSICAL PROPERTIES of SnCl_2Pc FILMS and $\text{SnCl}_2\text{Pc/PENTACENE}$ HETEROSTRUCTURES

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Phthalocyanines are one of the most stable and photosensitive organic semiconductors [1] and for a long time are widely used for a creation of photoconverters and solar cells as p-type component [2]. In contrast to majority of organic semiconductors, dichlorotin phthalocyanine (SnCl_2Pc) is n-type semiconductor [3]. And SnCl_2Pc conductivity is 1-3 orders larger than most of others phthalocyanines [4]. Therefore, SnCl_2Pc films are expected to be perspective component for development of photosensitive p-n type organic heterostructures and solar cells. Furthermore, cubic nonlinear optical susceptibility $\chi^{(3)}$ of SnCl_2Pc films is about order greater than one of other phthalocyanines films [5].

The CT-states transitions of planar phthalocyanine molecules are forbidden on symmetry and can be observed in electroabsorption spectra only. However, probability of CT-states transition for non-planar phthalocyanine molecules strongly increases and these transitions can be observed in absorption and photovoltage spectra [6].

The optical and photovoltaic properties of SnCl_2Pc films and $\text{SnCl}_2\text{Pc/pentacene}$ heterostructures have been studied. The weak bands at 1.35, 1.52 and 2.05 eV have been found in absorption and photomodulated reflectance spectra of SnCl_2Pc films. These bands aren't associated with absorption of molecules and can be caused by charge transfer state formation in SnCl_2Pc films. The formation of these states is a result of *hydrogen-like* interaction of Cl atoms of one molecule with peripheral H-C atoms of phthalocyanine rings of another molecule.

The low concentration of the recombination centers of charge carriers is formed on free surface of SnCl_2Pc films. The formation of these centers can be caused by adsorption of molecules of air (for example, oxygen). And this concentration essentially decreases at air evacuation before pentacene layer deposition in vacuum. In the consequence, the interface with insignificant charge carriers recombination rate is formed between SnCl_2Pc and pentacene layers. Therefore, p-n type $\text{SnCl}_2\text{Pc/pentacene}$ heterostructures are perspective for development of organic photoconverters, including solar cells.

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NEGATIVE PHOTODIELECTRICAL EFFECT IN TWO-LAYER STRUCTURES "MODIFIED C₆₀ FILMS – FERROELECTRICAL LIQUID CRYSTAL"

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Within the range of 10^{-3} to 10^6 Hz investigated were the frequency dependences of capacitance C and resistance R of two-layer structures "modified C₆₀ films - ferroelectrical liquid crystal (FLC)". Measurements were taken in darkness and on exposure to focused white light of halogen incandescent lamps. The FLC side was exposed to light. The density of the light energy equals $1,5 \text{ W/cm}^2$.

Preliminary (before the measurements of C and R), modification of C₆₀ films properties was performed using two methods: the irradiation of the Kr-F the laser at the wavelength of 248 nm [1] and treatment with the amine vapor (1,8-octanediamine) [2]. A thickness of the fullerene films was equal to 100 nm.

As was shown in [3], such films in a contact to glycerin have a high photosensitivity with the ratios C_P/C_D and R_D/R_P (the index D corresponds to measurements in darkness, P - on illumination) having the peaks. Heights of these peaks (≈ 6 for C and ≈ 20 for R) and frequency position (300-5000 Hz for C and 5-70 Hz for R) depend on a method modification of the C_{60} films.

In the C_{60} - FLC structures, the ratios C_P/C_D and R_D/R_P one order lower and their values for all the phases (cholesteric, smectic A and particularly in smectic C*) increased with decreasing the frequency. At the temperatures that corresponded to the smectic C*-phase, but closer to transition into a solid state, observed was an effect of increasing the capacitance on exposure to light (negative photodielectrical effect) while the R_D/R_P was more than unit (the same as in other phases). The revealed effect was characterized by the weak dependence C_P/C_D on a modification method of fullerene.

The analysis of the frequency dependences C_P/C_D has shown that, at the frequencies $\approx 2 \cdot 10^{-3}$ Hz, the negative photodielectrical effect disappeared and, with further decreasing the frequency, observed was an increase in capacitance under illumination, which was common for other phases.

Researches were carried out in cooperation Universidad Nacional Autonoma de Mexico (Mexico) and financially supported by the budgetary theme 1.4.1 B/109 of the Institute of Physics, NAS of Ukraine.

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EFFECT OF COMPOSITE LAYERS BASED ON DYES WITH DIFFERENT TYPE OF CONDUCTIVITY ON PHOTOVOLTAIC PROPERTIES OF CIS FILMS

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We considered polymers and organic semiconductors as perspective materials for the CdS replacement because of presence of toxic Cd in heterostructures CdS/CuInS₂ (CIS), for which the efficiency of a transformation more than 17 % was obtained. However, preliminary studies have shown, that after the deposition of polymeric layers PEDOT-PSS and 3-I-octylmetacrylate (3-I-VC-OMA) on a free surface of n-type CIS simultaneously there is a small decrease photovoltage (V) and essential increase short circuit photocurrent (Isc) [1].

It is possible to explain this by the decrease of potential barrier height and magnification of the efficiency of charge carriers transport through the CISCuT/PEDOT-PSS interface. The value of V and Isc change depends on molecular structure of a polymeric compound. However it does not result in change of spectral dependence of V and Isc. Hence, on CISCuT/polymer interface is maintained great concentration of trap centers and high rate of a surface recombination of charge carriers in CIS layer, which gives in essential decrease of a photosensitivity of heterostructures at $h\nu > 2.4$ eV [2]. At the same time at the deposition on a free surface CIS layer of organic dye there is a partial neutralization of trap centers and decrease of a recombination rate of charge carriers at the interface with CIS [1,2].

The aim of the present work was to study the influence of composite layers polymer/dye with different conductivity type on photovoltaic properties of CIS based structures.

The introducing dye in a polymeric compound can lead both to V increase, stimulated by the increase of potential barrier height and to neutralization of centers of a recombination of charge carriers at the interface owing to interaction of molecules of dye and CIS.

It is stated, that the effect of influence of dye introduction depends both on a material of polymer and on the type of dye conductivity. Hexaindoletricarboyanine dye (HITC, p-type) introducing in 3-I-VC-OMA leads to V increase in 1.5-2.0 eV region (range of strong absorbance and maximal photosensitivity of HITC composites), and practically doesn't change spectral dependence of V in the region of 2-3 eV (the region of strong influence of recombination centers of charge carriers at a surface CIS). Therefore, the increase

of V occurs with help a photogeneration of charge carriers in the composite layer, and thus there is no neutralization of surface centers of a recombination at a surface of CIS film.

The deposition of composites of HITC with polyepoxypropylcarbazole (PEPK) gives in essential decrease of V in wide spectral range. V increase is observed only at $E \sim 2.25$ eV. PEPK molecules can first and more effectively precipitate on CIS free surface, that will neutralize V increase in the field of HITC absorption, and the rise at ~ 2.25 eV can be associated to more effective aggregation of the dye in this polymer (aggregates can have the greater quantum yield of photogeneration that single molecules). Methyl perylene pigment (MPP, n-type) introducing in both 3-I-VC-OMA, and PEPK polymers gives in decrease of V in 1.5-2.7 eV range. Probably, there is a predominant precipitation of MPP molecules on CIS surface that leads to decrease of potential barrier height at CIS/composite interface.

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NANOMETER SCALE MODIFICATIONS OF THE Si/SiO₂ SURFACE BY SCANNING TUNNELING MICROSCOPE

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Si/SiO₂ interfaces possess unique electronic properties. The peculiarities of charge accumulation and transfer near this boundary realize a wide range of semiconductor devices. However, processes redistribution a charge on Si/SiO₂ interfaces keep not clear.

One of the most convenient methods for research and registration the charge redistribution processes into Si-SiO₂ interfaces is the scanning tunnel microscopy technique (STM).

The aim of this work was to study the mechanism of silicon surface modification using the STM-method in air depending of scanning parameters.

The polished plates of silicon p - type were used for experiment. The surface of species was not subjected to any additional treatment. There was a native oxide layer by thickness about several nanometers on a surface of silicon in this case.

The work was carried out an scanning multimicroscope SMM- 2000T, which is intended for realization of researches on air, resolution on coordinate along a surface up to 0.3 nm, on an axis z , perpendicular surface, up to 0.1 nm. A range of change of a tunnel current I - from 0.01 up to 160 A, a range of a voltage U on the interval a probe - sample - from 0 up to $\pm 10V$. The probe was prepared by the oblique cutting of a copper wire.

Fig.1 presents the STM image of the modified areas.

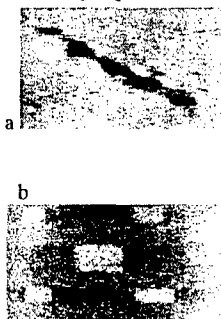


Fig. 1. The STM image of the silicon modified under: a) a positive voltage on a sample (modification voltage $U_{mod} = + 5V$, visualization voltage $U_{vis} = + 4.5V$); b) a negative voltage (modification in the left top corner at $U_{mod} = -4.4V$, each subsequent modification was carried out with increase of a voltage on 0.4V, greatest voltage of modification $U_{mod} = -6V$ in the left bottom corner of a snapshot. $U_{vis} = -4V$)

The sequence reception of the modified areas was carried out in the following order: a small site of a surface (mode of modification) at first was scanned, then scanning a site of the increased size was made which includes the modified site (mode of visualization). The modification of a surface occurs if the appendix voltage above than some threshold meaning $U_{thr} = 3V$. It is necessary to note, what the best quality STM image of a surface is observed provided that the modification voltage exceeds a visualization voltage on $U = 0.4V$.

Shown that the character of modification depends on polarity of the applied voltage (at negative polarity on a sample are formed a protrusions, at positive polarity are formed a cavities). The change of a surface morphology has a charging nature. The surface modification of a sample occurs under condition of excess of the applied voltage of some threshold meaning ($U_{thr} = 3V$).

GIANT MAGNETO RESISTANCE IN THE POLYMER-FERROMAGNETIC SYSTEM

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The aim of this work was to investigate the influence of outside magnetic field on electron transport in the asymmetric layer structure magnetic metal/polymer/non-magnetic metal type.

Magnet electrode has been made of Fe-plate and Ni-plate with opposite in sing of magnetostriction factor. Copper has been used as non-magnetic metal and second electrode. Polymer film has been made with the help of spin-coating technique. Polymers were chosen from the class of polyarylenephthalides. Sample

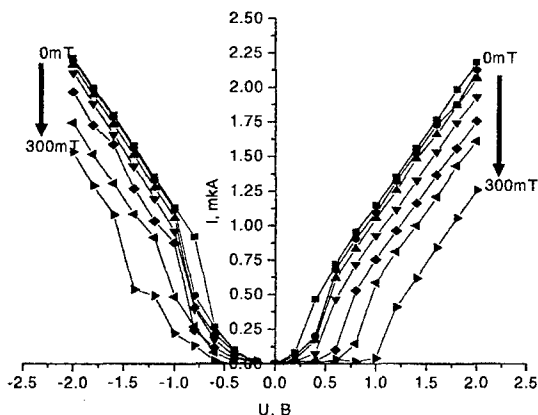


Fig.1. Current-voltage characteristics of Fe-Ni-polymer-Cu structure with a different value of magnetic induction (0 – 300 mT). Arrows showed direction of magnetic field increase by step 50 mT.

was put into homogenous magnetic field during the experiment. It was changed in the interval from 0 to 300 mT at room temperature. Current dependence from value of magnetic field was measured in the experiment. The initial condition of sample was corresponding to high-conducting state. the sample conductivity didn't change when the level of magnet field was increased up to ~160 mT. Then we observed stepwise decrease of current at the increase of the magnetic field higher than this critical point and the sample actually moved on to low-conductive state. At the decrease of magnetic field a backward transference into high-conducting state takes place but at a lower level of about 140mT. That hysteresis was observed. Relative change of resistance is $\sim 10^6$ - 10^8 times. To establish the reasons

of such influence of the magnetic field on charge transfer in experimental structure magnetic-polymer-non-magnetic metal current-voltage characteristics (CVC) were investigated with a different value of magnetic induction (Fig.1). It was studied the influence of current direct to the value of magnetoresistance phenomena. It was established that GMR a strong dependence from the current direction.

RADIATION-ENHANCED CHANGE OF ELECTRON PARAMETERS OF POLYMERIC SOLAR CELL WITH FULLEREN-DERIVATIVE COMPOSITE

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Using of photoinduced ultrafast charge transfer in polymer/fullerene system allow to increase the efficiency of solar cell with fullerenderivative composite polymer up to 3.5 %. This magnitude is considerably higher then conversion in other polymer cells [1]. Earlier we were shown the efficiency of the microwave treatment for improvement of electron parameters of MIS structures and Schottky diodes [2, 3]. The objective of this work was investigation of the effect of microwave radiation on electron parameters of photoactive layer in polymer solar cell. It was composed of fullerenderivative polymer PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) with adding of the polymer P3HT [poly(3-hexylthiophene)] to weight relation of PCBM: P3HT = 2:1. The blend was deposited on Ti-coated (thickness 40 nm) *n*-type silicon substrate. Active layer thickness was equivalent 80-100 nm. Its metallization was realized through mask with square and round holes by thermal evaporation of Ti or Au in vacuum. The samples were exposed to magnetron microwave radiation (frequency $f = 2.45$ GHz, power 1.5 W/cm^2 , processing duration not exceed 10 s).

For control of electron parameters of initial and irradiated structures were applied method of the tetra-line measurement of metal-polymer resistance and electroreflectance modulation spectroscopy. Electroreflectance measurements were made at room temperature in the energy range at 3.6 eV that correspond to

band-gap energy of PCBM semiconductor polymer. There were determined energy E_g , the value of the phenomenological broadening parameter Γ and energy time relaxation $\tau = \hbar/\Gamma$. It was ascertained that with grow of the irradiation time the summary resistance of metal-polymer structure decreases and efficiency of this decreasing like the initial resistance depend on metallization type (Ti, Au). Time of the irradiation also had an influence on spread of the values of the resistance on polymer area. It decreased with the increase of the irradiation time. The results denote advantage of using titan ohmic contact in such solar cell. Analysis of the elerctroreflectance spectra shown that transition energy is decreased from 3.69 eV to 3.62 eV after microwave irradiation. The phenomenological broadening parameter (it describe the scattering of light excited charge carrier in active layer) was decreased from 84 meV to 71 meV and τ increase from $7.8 \cdot 10^{-15}$ s to $9.3 \cdot 10^{-15}$ s.

The results obtained were explained: i) by effect of radiation-stimulated interdiffusion in metal-polymer interface that conduce to improvement of the ohmic contact electron properties; ii) by structural ordering of the composite polymer volume under influence of the microwave treatment; iii) by decrease of the intrinsic stress in it and increase of its homogeneity after irradiation. The structural ordering of the composite polymer volume is confirmed by appearance of the electroreflectance signal from silicon substrate under active layer at energy region near 3.4 eV after irradiation that could not be registered in unirradiated disordered structure.

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PHOTOCAPACITANCE EFFECT IN THIN FILM PYROELECTRIC ORGANIC POLYCYCLIC COMPOUNDS

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Organic diphenyl compounds are widely used for practical application. Due to pyroeffect existence, the 4-nitro-4'-aminodiphenyl has high sensitivity to the changes in the environment temperature.

In order to understand better the practical possibilities of this compound, the data of its fundamental parameters are needed, which are still absent. Therefore, the investigation of dielectric relaxation processes in the 4-nitro-4'-aminodiphenyl layers has been conducted in the frequency range of electrical fields from 10 Hz to 100 kHz at the temperature range of 15-60 °C. The research carried out indicates on the possibilities if their application as optoelectronic sensor.

By using the measuring system based on Gen Rad 1621, Datron 1065 and Gould-Bryans S50000, allowing measurement the changes in the capacity $\Delta C \sim 10^{-8}$ order from nominal value of C ($C \sim 100$ pF), the photocapacitance effect is detected. The measured spectral distribution ΔC in the range of wavelengths of photoexiting of 300-800 nm is agreed well with spectral distribution of photocurrency. The temperature dependence of the kinetic of $\Delta C = \Delta C(t)$ of photocapacitance effect in the on- and off- photoexiting regime has been studied in the vicinity of maximum of sensitivity $\Delta C = \Delta C(\lambda)$ ($\lambda_{\max} = 550$ nm). It is established that in the on- photoexiting regime, when $t < t_0$ (t_0 depends on the temperature as well as wavelengths of photoexiting), the kinetic of ΔC is described by two exponential functions with different relaxation times, τ . The energy of temperature activation of more long-time τ values is determined, $\Delta E_{\text{on}} = (0.7 \pm 0.1)$ eV. When $t > t_0$, $\Delta C = \Delta C(t)$ dependence is described by the n -degree dependence, explaining by the appearance of the photoelectric state. It is determined that in the case of photoexiting, the kinetic of photocapacitance is described by $\Delta C = \Delta C_0 \exp -(t/\tau)^n$. The activation energy of optimal relaxation time $\Delta E_{\text{on}} = (0.7 \pm 0.1)$ eV is established.

The results obtained for the 4-nitro-4'-aminodiphenyl layers studied can be explained by the interconnection of the diphenyl bases with nitro- and amino-groups at the photoexiting, and the model, connecting the pyro- and photocapacitance effects, is proposed.

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TEMPERATURE EFFECT ON THE HYDROGEN BOND SYSTEM IN TRIBLOCK COPOLYMERS CONTEINING POLY(ETHYLENE OXIDE) AND POLYACRYLAMIDE

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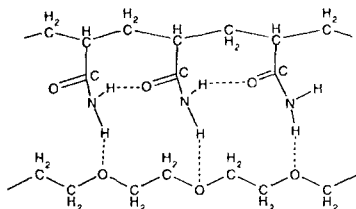
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Block and graft copolymers with interacting polymer components, which were called as intramolecular polycomplexes (IntraPCs), are intensive investigated in recent years. Hydrogen-bound IntraPCs can potentially be used as high efficient flocculants, different binders, polymer carriers in drug delivery systems. In the present work the triblock copolymers including polyacrylamide and poly(ethylene oxide) (PAA-*b*-PEO-*b*-PAA) with the different length of the polymer blocks, which are capable to interact with each other by hydrogen bonds, were studied. The temperature factor on the hydrogen bond system stability was considered also. Existence of the hydrogen bond system between different polymer blocks in PAA-*b*-PEO-*b*-PAA and their destruction under the temperature action were investigated by FTIR IR spectroscopy in the temperature region 25÷200°C. It has been used two PAA-*b*-PEO-*b*-PAA samples with $M_{\text{PEO}}=4 \cdot 10^4$ and $1 \cdot 10^5$ and also with $M_{\text{PAA}}=3.18 \cdot 10^5$ and $9.07 \cdot 10^5$ correspondingly. The samples of individual polymers with $M_{\text{PAA}}=6.31 \cdot 10^5$ and $M_{\text{PEO}}=4 \cdot 10^4$ have been chosen for comparison. Formation of the H-bond system between different polymer blocks is proved first of all by the low-frequency displacement (in 23 cm^{-1}) of the $\nu_{\text{C-O-C}}$ vibration band of PEO in the PAA-*b*-PEO-*b*-PAA spectrum comparing with position of the same band in the spectrum of individual PEO. In order to establish the H-bond structures of amide groups in the triblock copolymers comparing with individual PAA the computer division of the overlapped amide I bands using the spline method was carried out. It was established that there are relatively lesser of *cis-trans* and also

trans-associates of amide groups in the PAA-*b*-PEO-*b*-PAA samples than in individual PAA. At the same time the effective length of *trans*-multimers of amide groups in the block copolymers are higher unlike to PAA. Increasing of rigidity of PAA chains in the triblock copolymers can be explained by a participation of the *trans*-multimers in the formation of H-bond system between PEO and PAA segments:



It was shown that these H-bonds in PAA-*b*-PEO-*b*-PAA are stable in the wide temperature region ($25^{\circ}\text{C} < T < 170^{\circ}\text{C}$). Moreover only insignificant destruction of H-bonds between PAA and PEO and also in the *cis-trans*- and *trans*-multimers of amide groups in the triblock copolymers was revealed at $T \geq 170^{\circ}\text{C}$. Thus it has been established that given triblock copolymers form IntraPCs, which molecular architecture is stable to the temperature increasing.

IMPEDANCE SPECTROSCOPY STUDIES OF THE CHARGE TRANSPORT IN THE ELECTROCHROMIC POLYMER LAYERS

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The wide application of the organic optoelectronic devices based on the conducting polymers (electrochromic displays, indicators, electrochromic windows) arise a task to increase their quick-action and stability by the optimization of the charge transport across the film in proton electrolyte. Such devices based on electrochromic effect – changing in optical spectra (and color) in organic polymer layer under external electric field [1,2]. To study a mechanism of charge transport processes, which take place during the electrochromic transition in polyaminoarene layers the spectro-electrochemical behavior and impedance characteristics of electrochromic layers on the transparent ITO, SnO₂ electrodes have been studied in aqueous, organic and polymer electrolytes. Optical absorption

band positions of the polymer films (λ_{\max} = 380-400; 650-670 and 760-780 nm) depend on applied potential (E) in the interval of $E = -0,5...+0,5$ V (Pt/H₂). It has been found that a most significant electrochromic effect is observed in 0,01M solution of the perchlorate and sulfuric acids, a highest stability of colored – colorless transition observed in the mixed alcohol – aqueous solution of 0,1M LiClO₄ at pH = 3-4. Based on the data of impedance spectroscopy the effective diffusion coefficients of charge transport across the poly-o-toluidine, poly-o-methoxyaniline and polyaniline films have been defined ($D_{eff} = 10^{-9}-10^{-10}$ cm²/s) that give a possibility to estimate a transition diffusion time in electrochromic films ($\tau_d=0,02-0,5$ s). The measured components of impedance indicate the dominant role of the structure of the polymer matrix in the limitation of electron transport rate.

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ALKALINE HYDROLYSIS OF GRAFT COPOLYMERS DEXTRAN-POLYACRYLAMIDE. EFFECT OF COPOLYMER MOLECULAR STRUCTURE ON THE CONVERSION DEGREE

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Modified polymers can be obtained by post-modification of materials, which are difficult to synthesise by direct polymerization of the corresponding monomers. For example, partially hydrolysed polyacrylamide having the better flocculating behaviour that polyacrylamide itself can be prepared by hydrolysis enough easy. It was shown that graft copolymers based on polysaccharide and polyacrylamide exhibit much better flocculation characteristics than the conventional polysaccharide and synthetic polymer-based flocculants. Obviously, these systems should be very interesting due to possibility to obtain different samples with partially hydrolysed grafted chains. However until now the influence of the intramolecular structure of graft copolymers on the degree of transformation during alkaline hydrolysis did not investigate.

The aim of present work is in the preparing of high efficient flocculating agent based on Dextran-graft Polyacrylamide with special emphasis on copolymer molecular structure effect on the alkaline hydrolysis process.

Two samples of graft copolymers based on dextran ($M_w=20000$; $M_w=70000$) graft Polyacrylamide were synthesized using ceric-ion-reduced redox initiation method. Molecular parameters of graft copolymers were determined by light scattering, viscometry, GPC and X-ray diffraction. It was shown that their macromolecular structure strongly depends on the molecular weight of Dextran component. The anionic derivatives of these copolymers were obtained by the alkaline hydrolysis. It was established that the degree of copolymers modification depends on the conformation of grafted polyacrylamide chains. It was shown that intramolecular structure namely the conformation of grafted polyacrylamide chains influences on the kinetics of hydrolysis and on the degree of amide groups conversion.

Acknowledgements

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ELECTRO-OPTICAL CHARACTERISTICS OF VACUUM DEPOSITED CONDUCTIVE POLYMER FILMS

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Polyaniline (PAN) and poly(p-phenylene) (PPP) thin films were prepared by vacuum deposition from powder. UV-Vis absorption, infrared and photoluminescence spectroscopy of the deposited films have been studied. The photoluminescence spectrum of the vacuum deposited PPP films shower peak at about 521 nm. The optical absorption spectrum of PAN shower the wide peak at 400-450 nm that correspond PAN in the completely reduced leucoemeraldine state. By the laser ellipsometry methods were defined that the vacuum deposited PAN films on the silicone substrates have an optical anisotropy. Due to increasing of deposition temperature the anisotropy decreasing. The electrochromic element with PAN films is development that characterized by presence of stable optical memory and high contrast ratio.

COLLECTIVE BEHAVIOR OF COLLOIDAL PARTICLES IN NEMATIC LIQUID CRYSTALS

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The nature of the interaction between objects in nematic liquid crystals has so far been studied both theoretically and experimentally. The theoretical studies have been concentrated mainly on two-body interactions, neglecting many-body corrections, and using either analytical or fully numerical approach. The analytical, in most cases multipole-expansion approach, is expected to be valid in the far-field regime, i.e. at large interparticle separations, where the perturbation of the inclusions is small. In this picture, the object in a liquid crystal is considered as a static source of either monopole, dipole or quadrupole field that interacts in a pairwise manner with another object in its vicinity. This approach is therefore analogous to the multipole interaction picture in electrostatics and predicts $1/r^2$ structural force between two monopoles, $1/r^4$ structural force between two dipolar-like objects, and $1/r^6$ force between two topological quadrupoles. In comparison, fully numerical approach, found a good agreement for two parallel dipoles generating $1/r^4$ attractive force, whereas for two antiparallel dipoles, the numerically calculated repulsive force was stronger than expected from analytical considerations, $1/r^3$. The clear theoretical argument for the breakdown of the analytical approach is not available at this time, but is an indication of its limited validity.

We demonstrate a variety of ordered patterns, including hexagonal structures and chains, formed by colloidal particles (droplets) at the free surface of a nematic liquid crystal. The surface placement introduces a new type of particle interaction as compared to particles entirely in the LC bulk. Namely, director deformations caused by the particle lead to distortions of the interface and thus to capillary attraction. The elastic-capillary coupling is strong enough to remain relevant even at the micron scale when its buoyancy-capillary counterpart becomes irrelevant.

We report an unusual mechanism of laser trapping and manipulation of small colloids in the nematic liquid crystal. In that experiment, micron-sized glass particles with homeotropic boundary conditions were dispersed in the nematic liquid crystal with refractive indices that were larger compared to the index of refraction of colloids. Under such conditions, a repulsive force is expected to arise between a strongly focused light and the colloidal particle. As a surprise, the opposite was clearly observed : the colloid was attracted into the laser focus (trap) over extraordinary large separations of several microns. We first give a detailed description of the laser tweezers experiments followed by an extensive analysis of the observed trajectories of the colloids during many trapping experiments for different laser power. This is followed by an extensive analysis of the laser

trapping potential, which turns out to be highly anisotropic in space. For certain direction, we observe the Coulomb-like pair potential with an apparent $1/r$ separation dependence. In the theoretical section we present a numerical study of the interaction of the colloidal particle with a strongly focused laser light, where the laser-induced local Freedericksz transition is taken into account. We show that this scenario reproduces an effective $1/r$ dependence of the trapping potential in a certain direction very well.

We elaborate in detail the systematical model and experimental evidence of collective behavior for colloidal particles dispersed in nematic host.

LINEAR AND NONLINEAR OPTICS OF CONFINED CHIRAL LIQUID CRYSTALS

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The report will present optical properties of a chiral liquid crystal layer with finite strength of the surface anchoring under influence of varying external conditions. These may be the temperature [1,2], external electric or magnetic fields [2,3], mechanical actions [4] and so on. The main feature of the optical properties of the layer is that smooth variations of the external conditions may result in jump-wise changes of the optical properties and in a hysteresis of these changes being dependent on the thermal director fluctuations [5] when the variations of the external conditions are inversed. If the surface anchoring is not very strong the mentioned effects are directly connected to the shape of surface anchoring potential so there is possibility to restore the actual shape of surface anchoring potential from the corresponding experimental measurements. As a first step for restoring the actual shape of surface anchoring potential new model surface anchoring potentials (differing from Rapini- Papoular one) are introduced [6,7] and studied. The equilibrium optical properties and their hysteresis at varying temperature and external field, temporal dynamics of the jump-wise changes of the optical properties, singularity free walls between areas of LC cell prior and after a jump-wise change and the motion of these walls are presented as specific phenomena optical studies of which occur to be informative to the discussed problems. A special attention is paid to the director distribution in the Cano-Granjean wedge at weak anchoring where for a sufficiently short pitch CLC the well known defect lines separating the wedge area differing by the number of director half turns at the wedge thickness may be replaced by nonsingular walls.

The available experimental data on the problem are presented and the applied significance of the investigated phenomena is discussed .

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MOLECULAR DYNAMICS, SURFACE ANCHORING AND ELECTRO-OPTIC PROCESSES IN NEMATICS BY PHOTON CORRELATION SPECTROSCOPY

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The purpose of the present report is experimental investigation of molecular dynamics and anchoring of nematic liquid crystals with a solid surface by photon correlation spectroscopy. The technique is based on investigations of equilibrium thermal fluctuations and their quenching under surface influence and external ac electric field in the monocrystal regime.

Current theories of molecular light scattering are analysed for a proper choice of experimental technique, scattering geometries, high signal/noise ratio and the informativeness of measurements. All types of the tensor order parameter fluctuations were taken into account: i) transversal director fluctuations, ii) longitudinal and iii) local biaxial ones. The depolarized scattering from transversal fluctuations dominates for 0.6 μm waves; the scattering from the longitudinal fluctuations is polarised and strong at the wavelengths of 0.4 μm , and the biaxial fluctuations are expected to dominate for UV- and neutron scattering.

The experiments were performed on flat 20- and 40 μm -thick cells, as well as with wedge-shaped cells, where the thickness was varied from 5 to 40 μm . Planar and homeotropic molecular orientation was achieved respectively on PVA and with surfactants: i) cetyl trimetyl ammonium bromide (CTAB), ii) hydroquinone, and iii) cromolane. The orientation was controlled by the conosopic technique, n_e

and n_o refractive indices and their temperature dependencies were measured by interference fringes in a modified Rayleigh interferometer providing 0.001 accuracy, the dielectric constants were measured by tg δ - technique.

From these measurements following data were retrieved: the tensor order parameter modulus, orientational diffusion coefficients for splay, twist and bend deformations, Frank elastic constants K_{11} , K_{22} , K_{33} , six Leslie viscosity coefficients, polar and azimuthal components of the anchoring energy; the temperature behavior of each parameter was measured.

Possible sources of ambiguous interpretation of obtained results are analysed:

i) light-induced conformational changes of molecules, ii) changing of molecular tilt angle under temperature, iii) chemical stability of the samples under humidity, IR- or UV radiation.

In the photon correlation spectroscopy data are retrieved from the dynamic light scattering on natural thermal fluctuations, no reorientation in external field is required, so these measurements are undisturbing and more informative. All parameters were measured on the same cells, excluding uncertainties due to surface preparation, thus correspondence of molecular end chains symmetry and flexibility with the surface preparation influence can be established.

The theoretical models are performed using Matlab software and compared with experimentally obtained data.

STUDY OF A NEW DISCOTIC LIQUID CRYSTALS FOR PHOTONIC APPLICATIONS

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Discotic liquid crystals based on various aromatic cores such as triphenylene, phthalocyanine, tricycloquinazoline, etc. have recently emerged as a new class of fast photoconducting materials. Discotic molecules are also of interest for their intriguing supramolecular architectures. Their strong interactions within columns lead to potentially high charge-carrier mobilities, a property that is essential in the development of organic photovoltaic solar cells or transistors.

A family of novel discotic liquid crystals based on the 3,5-dicyanopyridine core with long side decoxy chains was synthesised and characterised. The specially designed liquid crystal cells with two different types of electrodes (ITO and aluminium) and with polyimide thin films (or without) were prepared. The time of flight (TOF) and degenerated two wave mixing (DTWM) experiments were performed with the use of these cells filled with the liquid crystal. The mobility of the holes was found to be of order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ being in agreement with literature data for this type of molecules.

The liquid crystal cells were also successfully used for holographic applications. The diffraction gratings were obtained with the use of the Ar⁺ laser and the dependence of the diffraction efficiency on different external parameters (laser power, geometry of the DTWM experiment, electric field, thickness of the LC cell) was measured. Obtained permanent gratings were then observed with the polarising microscope, after heating up to a temperature of the phase transition (Colh – isotropic) all modulations disappeared. A single laser beam illuminating the LC cell could also erase the gratings.

The mechanism of the recording and erasing of the gratings is not yet known but two hypotheses can be put forward: a temperature depending mechanism (based on disordering of the discotic liquid crystal phase into the isotropic phase by the heat of the laser beam) and a change of the induced dipole moment of the illuminated molecules. Both mechanisms are possible, further studies are necessary to establish the correct one.

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OPTOELECTRONIC PROPERTIES OF IONICALLY SELF-ASSEMBLED AZOMETHINE-BASED LIQUID CRYSTALS

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In this communication, we will report the synthesis and detailed chemical (¹H/¹³C NMR, Elemental Analysis, FTIR-ATR & SEC), thermal (DSC, POM & temperature-dependent (RT-473K) polarized FTIR-ATR), and optical (UV-Vis & PL) characterizations of two types (see Fig.1) of π -conjugated organic semiconductors (OSCs) for the field of organic/plastic (opto)electronics^[1]: Thermotropic liquid crystalline (LC) bis(azomethine) OSCs (LCBAZx) vs. ionically self-assembled^[2] thermotropic LC^[3-4] bis(azomethine)-alkylsulfonic acid supermolecules^[5-7] (ISALCBAZx) in which the side-groups (i.e. functionalized sulfonic acids (FSA): C₁₀H₂₁SO₃H) are connected to the LCBAZ's π -conjugated backbone by a non-covalent (ionic-type (acid-base)^[2]: protonation of the CH=N units by SO₃H groups of the FSA derivative used in this study) interaction.

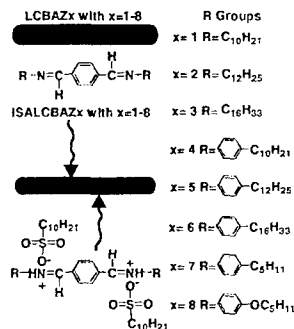


Fig.1: Chemical structures of "rod-shaped" LCBAZx molecules vs. Ionically Self-Assembled (ISA) "hairy rod-shaped" LCBAZx-C₁₀H₂₁SO₃H supermolecules.

Fig.1 and Table1 (solution PL features) show that some (8 over 16) of the members of this concise library of LC OSCs behave as thermostable^[8-9] "greenish emitters" leading to an overall tuning of the maximum of their emission bands over 42nm. Moreover, a closer look at Table1 shows that this modulation of their PL features is also resulting from controllable protonation-induced hypso-chromic shifts^[9] (of ca. 31nm vs. 16nm vs. 39nm for the selected cases of LCBAZx (x=4-6) vs. ISALCBAZx (x=4-6)). Finally, based on detailed thermal

LCBAZ molecules	$\lambda_{em,PL}^*$ [nm]	ISALCBAZ supermolecules	$\lambda_{em,PL}^*$ [nm]
LCBAZ4	538	ISALCBAZ4	507
LCBAZ5	532	ISALCBAZ5	516
LCBAZ6	535	ISALCBAZ6	496
LCBAZ7	-	ISALCBAZ7	502
LCBAZ8	-	ISALCBAZ8	509

Table1: Emission bands maxima ($\lambda_{em,PL}$ [nm]) extracted from PL (1.25*10⁻³M CHCl₃ solutions) measurements. *: Solution spectra recorded under a λ_{excit} = 400 nm excitation wavelength. -: PL signal "too weak" to be accurately analyzed with our PL set-up.

(sequence of phase transitions: *glass transitions, crystallization-melting, ordering-disordering of (smectic+nematic) mesophases, and isotropization*) vs. optical (UV-Vis & PL) characterizations, we will show how the complex LC behavior^[3-5] of these "smart" **LCBAZx/ISALCBAZx** organic semi-conductors is impacting their optoelectronic properties.

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NEW PHOTOALIGNMENT MATERIALS IN LCD'S DEVELOPMENT

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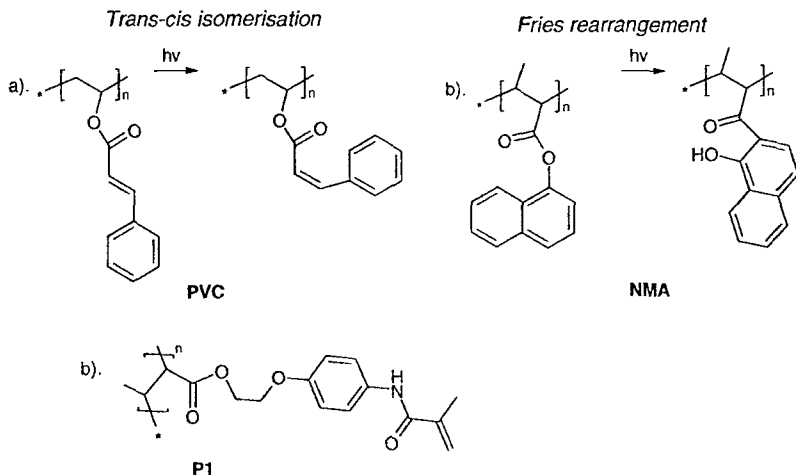
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Photoalignment can be realized by the use of azobenzene compounds, cinnamates, chalcones, stylobens, etc. From our point of view, in polymer films containing each of these organic compounds the reason of anisotropy formation generally is the same.

The first step of anisotropy formation is isomerisation of organic chromophore under the action of polarized UV-light. It could be *trans-cis* isomerization as in the case of cinnamates (as an example see reaction a. for **PVC**) or azobenzene compounds. The next step in some cases is further stabilization of the obtained anisotropy with photocrosslinking by UV-action. This stabilized anisotropy increases LC's alignment thermostability.

In our previous investigations [1] it was found a new material from the class of arylmethacrylates (1-naphthylmethacrylate, **NMA**) provided LC photoalignment due to the different isomerization reaction. The employed photoreaction was *Fries photo-rearrangement* (see reaction b.) which is a common reaction for all aromatic esters.



To prove the idea of a key role of *Fries photo-rearrangement* in arylmethacrylates was obtained polymer material **P1**. In contrast with **NMA** this material have no aryl ester photoactive center which could be able to undergo Fries photorearrangement.

No LC alignment was observed in cells prepared with substrate based on **P1** (UV-curing conditions were the same as for **NMA**) filled with nematic LC ZLI 2293 (Merck) and LC MJ961180 (Merck Japan).

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STUDY OF DYNAMIC AND NONLINEAR OPTICAL PROPERTIES OF POLYANILINE-FULLERENE-LIQUID CRYSTAL STRUCTURES

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Abstract: In the present paper the temporal characteristics of the polyaniline (PANI)-fullerene-nematic liquid crystal (LC) organic system have been studied. Such system could be applied in displays and optoelectronics. It has been noticed, that dealing with nanostructured medium based on fullerene-containing PANI sufficiently accelerates transitional processes in polymer-dispersed liquid crystal structure, causing mesophase reorientation in shorter times. It is supposed that the physical mechanism of accelerated sensitized nematic LC switching could be caused by intermolecular complex formation (see Fig.1) in conjugated polyaniline-fullerene organic system. This complex provokes an additional field gradient, the increased polarization and order-parameter rising. Quasi-transition from nematic to smectic phase has been observed. Registered switching times of the fullerene-containing nematic LC-systems are in the range of tens microseconds [1], which is not peculiar to the substance in nematic phase earlier have been observed in smectic phase only. In addition, nonlinear absorption of laser radiation in studied LC-systems has been established at wavelength of 1080 nm. This could be applied in human eye and optical device protecting systems.

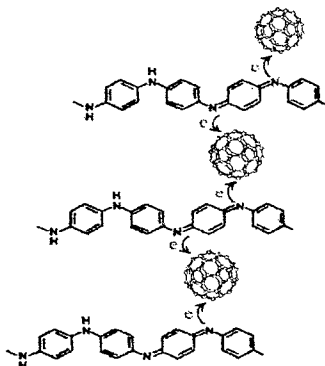


Fig 1. Possible scheme to form the polyaniline-fullerene complex

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PHASE DIAGRAMS AND STRUCTURE OF SALTED LYOTROPIC CHROMONIC LIQUID CRYSTALS

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Some types of aromatic molecules, such as trisulfoindanthrone (Blue 250) have ability to form lyotropic chromonic liquid crystal (LCLC) phase in a water solution. In this work, we present results of investigation of salt effect on phase behavior and structural parameters of LCLC phase of Blue 250. Adding different type of salt (inorganic, organic, sodium, potassium etc.) caused different effect on phase equilibrium. The investigation was provided for wide range of salts concentration from 0.05 mM up to 50 mM. The addition of sodium or potassium salts shifts the isotropic-nematic phase transition by several degrees, it allows us to move region of LCLC phase existence to the room temperature. Salt effects are predominantly dictated by rather the cation size than the anion. The presence of different salts influences the possibility of molecules aggregation in water solution.

EASY AXIS REORIENTATION UNDER LOW POWER VISIBLE LIGHT IRRADIATION IN A LYOTROPIC CHROMONIC LIQUID CRYSTALS.

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Effect of director reorientation under irradiation by linearly polarized low power laser light is for the first time reported for a lyotropic chromonematic. For a cell assembled with substrates covered by unidirectionally rubbed polyimide SE-7511 and filled with the chromonematic Blue 27 (5% by weight in water), the irradiation by the He-Ne ($\lambda=632.8\text{nm}$) laser produces a spot well visible with naked eye within which the orientation of the director is different from the original orientation. The studied chromonematic absorbs light with the maximum of the absorption band approximately at the $\lambda=640\text{nm}$ and this latter allows one for direct determination of the director orientation analyzing the light transmittance of the cell under the polarization microscope. We show time dependencies of the transmittance of linearly polarized light *in situ*, during the reorientation process. No changes of the spectra after the irradiation have been registered revealing the absence of photo-degradation as well as of changes in the

aggregates structure. The area with the reoriented director is found even if the cell was irradiated at the temperatures above the isotropic phase transition and then cooled down to the nematic phase. AFM scanning results for the surfaces of disassembled cells in irradiated and non-irradiated areas are analyzed.

PHOTOLUMINESCENCE OF LIQUID CRYSTALS CONFINED IN THE POROUS GLASSES

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The fluorescence (FL) spectra of the nematic liquid crystals *n*-butyl-*n*'-methoxyazoxybenzol (BMAOB) and *n*-pentyl-*n*'-cyanobiphenyl (5CB) introduced into porous glasses and coated on the quartz plates are investigated. It is obtained that the FL spectra of these LC in the layers and in the small pores are distinctly different.

For the BMAOB layer the band with maximum at 475 nm is observed. Additionally to this band, in the glass with a pore diameter $d=4$ nm the band at 550 nm is detected. With decreasing the pore size to 1 nm the band at 475 nm is completely suppressed and the band at 550 nm only remains. The latter band is assigned to excimer FL of azomolecules. The FL spectra of the BMAOB layer testify to effective molecular *trans-cis* photo-isomerization. At the same time, in the porous matrices another mechanism of photo-conversion prevails determined by confined geometry and interface influence [1].

In case of 5CB, the pore diameter decrease also leads to suppressing of the long-wave bands of FL spectra assigned to the pre-dimer and dimer couples of H-type. A spectrum of 5CB confined to small pores ($d<4$ nm) may be explained by superposition of FL from monomers, J-type dimers and 5CB associates with surface molecular groups of the pores. In this sense, porous glass acts as molecular sieve allowing only J-association of 5CB molecules [2].

This research was supported by NAS of Ukraine (grants VC89 and VC89-334).

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PHOTOLUMINESCENCE OF POROUS SILICON FILLED WITH LIQUID CRYSTAL 5CB

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The hybrid nanostructures based on inorganic and organic materials are intensively studied nowadays as perspective materials for optoelectronic emissive elements [1]. From the scientific point of view the energy exchange between the organic and inorganic components is especially interesting.

In the present research we consider nanoporous silicon filled with nematic liquid crystal *n*-pentyl-*n*'-cyanobiphenyl (5CB) as a specimen of hybrid systems with high quantum yield. The stationary and time resolved luminescence spectra of this system excited by nitrogen laser ($\lambda=337.1$ nm) were measured.

The maximum of the emission band for porous silicon was in the range 603-667 nm depending of sample morphology. In case of porous silicon filled with 5CB, along with bands of porous silicon, the short-wave excimer bands typical for 5CB were detected. The bands of 5CB and porous silicon were characterized by nanosecond and microsecond relaxation, respectively. It is revealed that filling with 5CB enhances luminescence of porous silicon in 2-3 times. Such enhancement is due to the energy transfer from 5CB to porous matrix. The possible mechanisms of energy transfer are discussed.

This research was supported by NAS of Ukraine (grants VC89 and VC89-334).

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ELECTRONIC PROPERTIES OF POLAR MOLECULES INTRODUCED TO LIQUID CRYSTAL MATRIX

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Aggregation properties of polar molecules embedded to liquid crystal matrix were studied using the time resolved PL spectroscopy. A different behavior of the molecules and aggregates in the PL spectra under external electric field was observed. The aggregation of the molecules leads to the enhancement of second harmonic generation.

Time-resolved photoluminescence (PL) spectra of organic dye molecules embedded to pentyl-cyanobiphenile (5CB) liquid crystal matrix have been studied

at one- and two-photon excitation. 4-nitro-4'-aminodiphenile (D-1) donor-acceptor molecule has intensive charge-transfer (CT) transitions in UV region. Liquid crystal (LC) cell with semi-transparent SnO_2 electrodes treated to provide homeotropic orientation of LC was prepared for spectral measurements.

If LC contains dye CT molecules dissolved in solvent under the concentration, which is less than 1 weight %, one can obtain clear and uniform solution in LC cell. Exciting at one-photon irradiation by argon laser at 337 nm, such compound shows PL of single D-1 molecules and of aggregates of these molecules. Both D-1 molecules aggregate's PL and second harmonic generation are registered under two-photon excitation at 1064 nm, and simultaneously there is no PL of single molecules. One-photon excited PL is attributed to intra- and inter-molecular CT, whereas PL observed at two-photon excitation, concerns generally an inter-molecular CT. When the concentration of D-1 molecules in LC matrix is increased over 1 weight %, dye molecules aggregates incorporate in colloid objects, which demonstrate intensive second harmonic generation at two-photon excitation.

PL spectra of LC cell show that external electric field changes the orientation not only of LC molecules, but also of single dye molecules as well as of dye aggregates.

ION ACCUMULATION AND RELAXATION NEAR MICROCONTACT TO LIQUID CRYSTAL IN $\text{Si}/\text{SiO}_2/\text{LC}/\text{ITO}$ STRUCTURE

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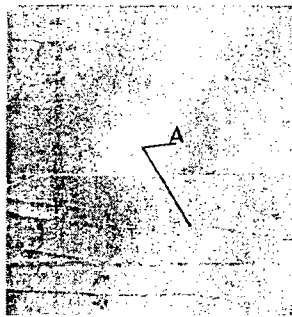
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We present the results of investigation the ion accumulation and relaxation in liquid crystal layer taking place in the vicinity of throughlike pore of dielectric layer SiO_2 (microcontact to liquid crystal layer) in $\text{Si}/\text{SiO}_2/\text{liquid crystal}/\text{ITO}$ structures. Charge accumulation within liquid crystal layer near microcontact occurs only under dc voltage of “-“ U polarity on Si substrate. Distribution of ion charge was studied by means of electrooptic effects near microcontact under low frequency ac voltage.

Fig.1 demonstrates a typical reorientation of hybrid nematic near microcontact in $\text{Si}/\text{SiO}_2/5\text{CB}/\text{ITO}$ structures under ac voltage. We can mark out two axial A and B regions respectively which show different behavior of pseudocolor change under control ac voltage. We suppose that two type negative charges are accumulated near microcontact which sufficient different by diffusion.

We stated also that accumulated charge causes the increasing of thresholds of planar-fingerprint texture, as well fingerprint – homeotrop texture transitions in comparison with the same thresholds far from microcontact. Difference between these thresholds can account several volts and strongly depends on 1) distance from microcontact 2) duration and value of dc voltage prior acted on structure, 3) frequency of AC voltage (at high frequency any difference is detected), 4) time of relaxation at AC voltage. The last takes several tens minutes. We believe that such ion induced bistability of threshold in cholesterics and such dependence on frequency can be used in display application. In this case a single pixel can be presented itself as round region of planar(or fingerprint/confocal) state with variable radius controlled by AC voltage.



We found that accumulated charge decreases the temperature driven a homeotrop-tilted transition in 5CB in the vicinity of microcontact. Such transition starts near microcontact at low temperature and axial-symmetrically propagates from microcontact with increasing of temperature that confirms axial distribution of charge. In present work we discuss the using of ion-temperature driven effect in nondestructive testing of thin films on silicon substrates.

Physical mechanism of space charge formation and relaxation is also discussed.

ELECTRICALLY CONTROLLED BISTABLE PHOTOSENSITIVITY IN Si/LC/ITO STRUCTURE.

Kucheev S.I.

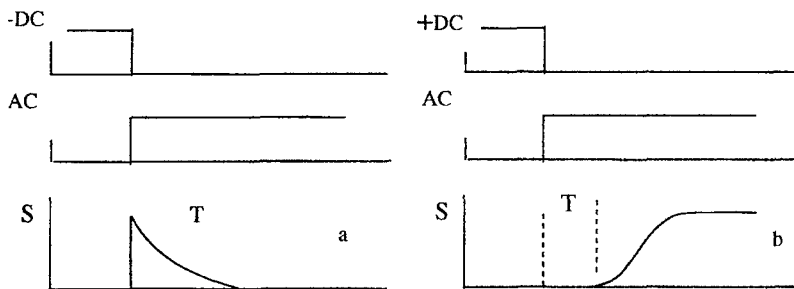
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In experiments the photosensitivity (S) of Si/5CB/ITO structure is investigated. As substrate the monocrystalline silicon of p-type conductivity with specific resistance equal to 4,5 Om*cm is used. Liquid crystal layer thickness was 5 mkm. ITO surface was covered by rubbed polyimide film to align homogenous the nematic. The photosensitivity of the structure is tested under AC voltage by He-Ne (0,63 mkm) laser illumination.

It is found that Si/5CB/ITO can be reversible switched from photosensitive state into no photosensitive one under the action of DC (within 5 B range) voltage

by appropriate polarity (Fig). Photosensitive state duration takes several days whereas no photosensitive state is significantly longer.



It is supposed that in no photosensitive state (a, Fig) silicon surface is clean therefore leakage current through Si/LC interface prevents depletion of silicon surface. In photosensitive state (b, Fig) the silicon surface is covered by ultrathin dielectric film¹ which is formed by DC action. This film limits a leakage current. It is also established that there is reversible change of liquid crystal orientation under DC action with appropriate polarity.

The role of ion charge accumulated near silicon surface in depletion layer formation is discussed. It is shown that duration (T) of photosensitivity relaxation (in the a case) and photosensitivity appearance delay (in the b case) due to ion influence on surface conductivity of silicon by field effect.

In the work the two interesting effects useful for application purpose are considered. First concerns with moving image contrast amplification by accumulated charge. In second case the effect of accumulation of charge near silicon surface in the structure under He-Ne laser illumination without external voltage action is considered.

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THE OPTICAL ELEMENT BASED ON PLANAR WAVEGUIDE WITH LIQUID CRYSTAL CORE

Z. Mykytyuk, A. Fechan, O.Sushynskyy, D.Volynjuk

The one of the important disadvantage of displaying information devices based on cholesteric-nematic effect is low contrast level. We propose the new constructive decision to dissolve this problem. The classic sandwich cell, witch

includes the correlation between the glass refraction index and the liquid crystal layer refraction index is the planar waveguide. Therefore, in liquid crystal layer (at the homeotropic texture) the light radiation, which propagated along the planar waveguide and scattered in perpendicularly to propagation direction, is a minimal. However, in liquid crystal layer the confocal texture is obtained due to voltage changing that leads to the light scattering. The light radiation flow is scattered evenly to all sides of cell, which provides the light transferring in perpendicular direction of planar waveguide. This constructive solution provides the increasing of contrast level. For inputting the light radiation into planar waveguide the prism, cylinder lens are used.

The volt-contrast characteristic behavior of the cholesteric-nematic transition is provided the wide range of grey level gradation in devices based on this effect.

The using in place of cholesteric-nematic transition the transition from Grangane texture to cholesteric confocal texture will permit to use this device work in inversion mode. This transition is given could be realized by control of applied device voltages. The dependences of the contrast value due to optical active dopant concentration, the angle and the method of the radiation inputting into liquid crystal cell are investigated.

CHOLESTERIC PITCH VARIATIONS AND HYSTERESIS PHENOMENA IN PLANAR LAYERS WITH NARROW ANCHORING POTENTIALS IN THE PRESENCE OF EXTERNAL FIELD

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Investigation of cholesteric liquid crystal pitch behavior for systems with constrained geometry in presence of external electric (magnetic) field and in the case of different model anchoring potentials at surface interface allows one to obtain valuable information on material properties useful for wide range of applications. It enables both to restore experimentally actual surface anchoring potential and to propose the way of layer interface processing in order to obtain certain features of field helix behavior.

Jump-wise variations of chiral LC pitch in thin LC layers for different shapes of the surface anchoring potential are present for temperature changes when the potential is not too strong [1,2]. These temperature variations depend

essentially on the form of angular potential. Similar dependence takes place for the cholesteric layer in the presence of external electric (magnetic) field [3]. The mechanism of the pitch jump is connected with slipping of the director at the layer surface through the surface anchoring potential barrier. New classes of model surface anchoring potentials were proposed [1,2], in particular, the potentials with a narrow angular width of the well [2], which lead to different types of pitch dependences in external field [3]. As it was shown in [4], in the case of narrow B-potential [2] for a definite interval of universal parameter $S_d = K_{22}/dW$, where K_{22} is the twist constant, W is the depth of the anchoring potential well and d is the layer thickness, the characteristic picture of helix variation in applied field, the double hysteresis curve with linear part, is present. In the present work theoretical comparison of hysteresis properties for Rapini-Papoula and B-potentials was performed. It was shown, that for the infinitely strong anchoring at one layer surface and finite strength of anchoring at the second field helix variations for these types of narrow anchoring potentials are qualitatively different. So, experimental cholesteric pitch measurements enable one to distinguish different forms of the angular anchoring potentials. The work is supported by the RFBR grant 06-02-16287.

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THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF SELECTED ROTAXANES

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Many original and interesting non linear optics phenomena for optoelectronic devices originate directly from the light induced and/or controlled mechanical motions at the molecular level. Molecules with mechanically interlocked components are promising structures for molecular machine – type applications because, in principle, they permit controlled, large amplitude, movement and positioning of one mechanically interlocked component with respect to another one. They fall into two classes: catenanes which consist of two or more interlocked rings and rotaxanes where a macrocycle is locked onto a linear thread by bulky “stoppers”.

In this paper we will present recent results of our studies of linear and nonlinear optical properties of selected rotaxanes. The linear optical properties of the rotaxanes solutions were studied by the UV-VIS spectroscopy and the nonlinear optical properties by harmonic generation and by polarization, Z-Scan and time resolved four wave mixing techniques.

LASING BY RANDOM AND REGULAR PHOTON CRYSTALS MADE OF DYED VESICULAR POLYMER

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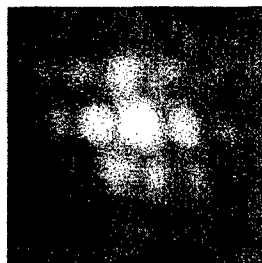
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Optical resonant modes in photon crystals (PhC) can be created by looping the photon trajectory or introducing a structural defect into the initially perfect PhC. Now exist the strong trend to design nanocavities based on the PhC [1]. Especially 2-D PhC slab structures have been widely studied when in the horizontal directions photons can be spatially localized by 2-D photonic bandgap effects while in the vertical direction they are confined through total internal reflection.[2, 3] After the first demonstration of the PhC nanocavity laser based on

a single removing air-hole by Caltech group [4], various cavity structures have been demonstrated. Recently, 2-D PhC cavities have drawn much attention as a promising candidate for cavity quantum electrodynamics experiments reporting vacuum Rabi splitting [5] and high-efficiency single photon sources [6].

We have come around the problem from study lasing of 3D random light scattering dyed polymer matrix where scattering centers have been created by the fumed silica or other solid particles with high relative index refraction [7]. The given report contents the results of study lasing in dyed vesicular polymer films where the scattering centers were created by N_2 -approximately 1 μ m size bubbles randomly distributed in volume in first case and regularly distributed in second case in film (see diffraction picture below). Long time ago we had realized and studied photon crystal laser where PhC matrix made of dyed cholesteric liquid crystal [7]. Nowadays we present fresh (and more complicated for understanding) results about origination the fine structure of lasing emission by vesicular dyed matrix at room and helium temperature. Mentioned complication results from the possible double-natured origination of fine structure in the case of lasing by random scattering matrix: first one due Anderson localization if condition $kl \approx 3.14$ equitable for given particle size and concentration and second – due to selective amplification of a weak structure presented in dye fluorescence emission at low temperature. Dyed regular air-hole polymer film was made by selforganization condition developed in collaboration with V. Bormashenko (Israel). Lasing emission in the conditions occurs to be more predictable but nevertheless more rich about information.



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MOLECULAR ORGANIC CRYSTALS DAST, MNA, POM IN THE FORM OF THIN CRYSTALLINE FILM AND NANOCRYSTALS COMPOSITION – THE NEW AND PROMISING MEDIUM FOR NLO APPLICATION,

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The process of “red” crystal modification of DAST nanocrystals growing at precipitation was investigated. Method based on precipitation from solution in surfactant presence and embedding into UV-cured matrix. This method is the logical sequential to the authors previous investigations in dye nanocrystals. The

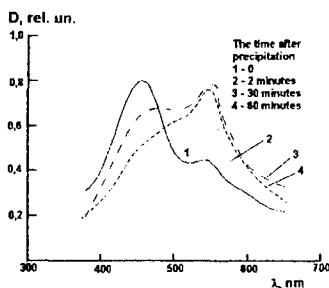
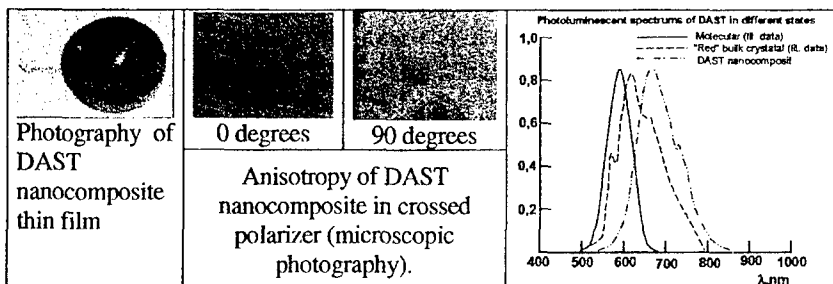


Fig. 1. Absorption spectrum of DAST nanocrystals

second-harmonic generation of produced crystals verifies their high nonlinear susceptibility. In the Fig 1. shown change of absorption spectrum of DAST nanocrystals during precipitation.

The new method of DAST nanocrystals fabrication in a UV-cured matrix based on the specific intermolecular interaction between DAST and polymer molecules in supersaturated methanol solution was developed. Method allows producing highly concentrated (up to 30%) nanocrystal-filled transparent composition. Nanocomposite is suitable to produce different photonics structures by soft lithography method. Formation of anisotropic nanocomposite by use of oriented polymeric matrix was investigated. The second-harmonic generation in very thin (about 1 mkm) layers confirms the high nonlinear susceptibility of this material. The photo, anisotropy and photo luminescent spectrum of new material shown in the next Fig.



The work was made under support of RFBR Project # 05-02-08048 "Investigation of electro-optic nanostructures with high hyperpolarizability based on nanocrystals density packing in polymer matrix for use in microwave optoelectronic elements" and Project of Russian Federal Agency of Education # 1.3.06 "Investigation of process of non-linear proprieties formation at transformation from molecular to nanocrystalline state of organic crystals"

NONLINEAR REFRACTION AND PULSED POLARIZATION RECORDING IN EPOXY POLYMER WITH AZOBENZENE

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Nonlinear refraction resulted from nonlinear optical (NLO) chromophore molecules orientation induced by laser pulsed excitation in a polymer structure based upon diglycidylether of bisphenol-A has been used for vector dynamic hologram recording. The polymer contains 4-aminoazobenzene as nonlinear optically active side groups covalently attached at each monomer unit. A one mode pulsed frequency doubled YAG:Nd⁺³ ($\lambda=532$ nm, $\tau_p = 10$ ns, $E_p = 1 \mu\text{J}$, TEM₀₀) laser has been used as a source of radiation.

The vector holograms were recorded by two orthogonally linear polarized laser beams. In this case the nonlinear medium responses to the modulation of the state of polarization of recording radiation rather than intensity modulation. As a result we could manage to separate out among a variety of competitive mechanisms of nonlinear refraction [1] taking place in the medium in question a contribution responsible for the polarization recording [2]. Efficient photoisomerization and reorientation processes results in a volume birefringence gratings. Value and dynamics of the induced refractive index anisotropy have been measured.

Recording of the gratings was investigated under different polarization combinations for the two writing beams. It was shown that in addition to vector gratings strong pressure gratings were recorded at some writing geometries due to polymer mass movement as a result of presence of a component of electric field gradient in the grating vector direction.

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NONLINEAR OPTICAL RESPONSE OF LIQUID CRYSTAL DOPED WITH ANTHRAQUINONE DYES

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It is known that an intensive light can cause a director reorientation in a nematic liquid crystal [1]. More than ten years ago Janossy with his collaborators discovered that just one percent of light-absorbing dye dopant dissolved in a nematic LC enhances this reorientation by a factor of hundred [2]. The proposed model [3] of this effect have assumed the light-excited dye molecules can changes the rotation diffusion constant of matrix molecules thus drastically increase reorientation ability. But the model gives only qualitative description and cannot explain series of experimental observation.

In this work, the nematic LC material, 4'-n-pentyl-4-cyanobiphenyl (5CB), was used. The LC material was doped with the anthraquinone-containing (AQ) non-azo dye. Experiments were performed for the $5 \div 150 \mu\text{m}$ cells with homeotropical and planar LC alignment. We studied AQ concentration dependences of the LC cells NLO response for the pulsed (femto-, pico- and nano-second ranges) and CW excitation [4] (He-Ne laser at 633 nm). Picosecond excitation at 532 nm in transparency range has given a possibility to readout the NLO response of the AQ dye subsystem in LC matrix. The obtained real and imaginary parts of a cubic NLO susceptibility versus the AQ concentration have essential nonlinear character. It reflects the dye molecules collective response impact on the laser selfaction effects. The more pronounced nonlinear concentration dependence of the LC cells NLO response was obtained with CW He-Ne laser excitation [5].

Effect of photoinduced refractive index variation sign inversion versus the orientation of the CW laser beam polarization towards to the director of a planar 5CB cell doped with non-azo AQ dye have been observed for the first time. At 50 degrees angle we observed a zero response of the NLO refractive index variation that changes to self-defocusing effect for parallel and self-focusing effect for perpendicular geometry of the polarization and the director.

A model of enhanced light-induced director reorientation based on the hypothesis of dye aggregation in a nematic liquid crystal was developed.

Theoretically predicted collective response of the excited molecules in the aggregates is in a good agreement with the experimental NLO response data.

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ANALYSIS OF BULK AND RELIEF GRATINGS IN PHOTOCHROMIC POLYMERS

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The photochromic polymers have been widely investigated in the last decade because of their potential use in various optical applications mainly in optical information storage and processing, polarization holography and in photonic devices [1,2]. Many of these applications rely on light-induced optical anisotropy occurring in many organic optical materials containing optically active units [3]. The azobenzene groups play a role of active units in photochromic polymers studied in this work. Optical anisotropy induced by polarized laser light is a consequence of an efficient reversible trans-cis-trans photoisomerization cycles of azobenzene groups and it can be investigated by holographic techniques.

We propose a simple model explaining the dynamics of photoinduced anisotropy during holographic grating recording in azobenzene functionalized polymers. The diffraction efficiency results from two phase gratings, i.e. a bulk refractive index grating and a surface relief grating [4]. The first one is connected with the index modulation Δn in the bulk of the material while the other results from film thickness modulation Δd observed at the surface of the azopolymer.

The first order diffraction efficiency $\eta_1(t) = I_{diff} / I_{input}$, as a function of recording time t , is discussed within model of two consecutive processes i.e. refractive index and relief grating build-up with the assumption of the phase shift $\Delta\phi$ between them. Additionally we assumed that $\Delta\phi$ is evolving with time. The

diffraction efficiency including contributions of refractive index grating Δn and surface relief grating Δd is calculated according to equation:

$$\eta_1(t) = J_1^2 \left\{ 2\pi \left[(\Delta n(t)d_0)^2 + (\Delta d(t)n_0)^2 + 2\Delta n(t)d_0\Delta d(t)n_0 \cos(\Delta\phi(t)) \right]^{1/2} / [\lambda \cos(\alpha)] \right\}.$$

Different shapes of the kinetics of holographic grating build-up monitored via power of 1-st order diffraction were calculated for various Δn , Δd and $\Delta\phi$ parameters. These calculations explain the complex dynamics of grating growth observed experimentally in azobenzene functionalized polymers during grating recording experiments.

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NLO EFFECTS IN POLYMERIC AZOESTERS

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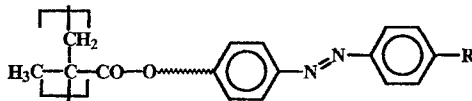
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The last decade observes increased interest to azopolymers, i.e. polymers containing azochromophores (usually, azobenzene derivatives) in the side or main polymer chain. The most attractive feature of azopolymers is an effective photoinduced optical anisotropy (POA), which reveals itself in a linear dichroism and photoinduced birefringence. This feature makes azopolymers rather attractive for a number of photonic applications such as polarization holography, optical memory, integrated optical circuits, and liquid crystal (LC) aligning substrates, *etc* [1,2].

In the present research we elucidate the ordering regularities in azopolymers on the polymethylmethacrylate (PMMA) base. This is the most popular class of

azopolymers quite attractive for practical uses because of enhanced thermal stability, excellent film forming properties, relatively simple synthesis, *etc.*

The new photochromic polymers and copolymers based on methacrylic azoesters were synthesized. The side chains of obtained polymers contain flexible alkyl spacers of different length and groups of different nature.



It was found that polymerization of corresponding azomonomers needs a long time, and the best polymer yields were obtained, when more than 10% (weight) of initiator were added. All monomers are able to copolymerization with methyl methacrylate. Synthesized polymers and copolymers are solids at room temperature and dissolved in benzene, toluene, dichloroethane, dioxane.

We apply transmission null ellipsometry supported by the modified total absorption method to study the 3D order in a big series of PMMA containing azofragments. This combination is effective and practical tool for the study of the orientational molecular distributions [3]. We consider the induced orientational order as a function of molecular structure, supramolecular organization and irradiation conditions. The regularities obtained are compared with those earlier established for other kinds of azopolymers.

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DETERMINATION OF THE HIGHER-ORDER NONLINEAR OPTICAL SUSCEPTIBILITY OF COMPLEX ORGANIC COMPOUNDS BY METHODS OF MULTIWAVE MIXING

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With increasing use of high-power laser sources it has been found that due to the interaction between high-power radiation and the matter the majority of materials can reveal not only the cubic nonlinearity but also nonlinearities of the fifth and higher orders. Besides, as a result of expanding the medium susceptibility into a series of dynamic grating components, new components emerge offering the possibility for the second- and higher-order Bragg diffraction of a reading-beam.

In this paper the possibilities of using the frequency-degenerate multiwave mixing schemes for measurements of the fifth- and higher-order nonlinearities were analyzed. According to the condition of Bragg diffraction for various spatial components of the grating, diffraction of different orders was realized from volume dynamic holograms due to changes in the propagation direction of a reading wave. Comparison between the experimental and theoretical data makes it possible to relate unambiguously the energy efficiency of multiwave mixing to the nonlinear susceptibility. The measurement conditions for the higher-order nonlinear optical susceptibility were optimized, to permit separation of the contributions made by the nonlinearities differing in order and to improve the measurement accuracy.

Efficiency of the proposed mixing schemes was tested experimentally on the basis of dye solutions in conditions of pulsed laser excitation. To separate the contributions of various nonlinearity mechanisms, the schemes with a delay between recording and reading pulses were used together with the schemes characterized by a variable period of holographic gratings. As an illustration, the figure below demonstrates the diffraction efficiency of dynamic holograms as a function of the signal-wave delay time, with respect to the reference waves on four-wave mixing with counter-propagating waves realized in the Rhodamine 6G dye solution. The appearance of two maxima may be attributed to the fulfilled condition of the coherent wave summation, separately for transmission and

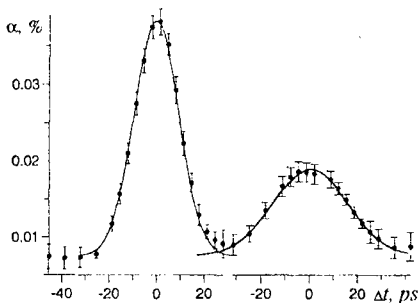


Fig. Diffraction efficiency as a function of the delay time of a signal wave

reflection dynamic gratings. Different values of the diffraction efficiency for gratings of these two types are caused by differing lifetimes of the thermal component of a nonlinear change in the refractive index. Proceeding from the obtained data, the values of the cubic optical susceptibility were calculated and the resonance-to-thermal contributions ratio for dynamic gratings was estimated. Based on similar schemes for six- and eight-wave mixing, the fifth- and seventh-order optical susceptibilities were measured.

THE ELECTRONIC AND NONLINEAR OPTICAL PROPERTIES (NLO) OF SOME PHENYLAZINE MOLECULES

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Biphenyl and bithiophene like π -conjugated molecules have attracted much attention due to their potentiality as a materials with nonlinear optical (NLO) properties[1-4].

In this study, the structural parameters, electronic and nonlinear optical properties of some phenylazines were calculated by using Becke three parameter functional (B3LYP) hybrid approaches within the density functional theory (DFT). All of calculations calculated with the 6-31++G(d,p) basis set, and via the GAUSSIAN 98W.

Furthermore, static polarizability (α), anisotropic polarizability ($\Delta\alpha$) and static hyperpolarizabilities (β) are calculated as a function of dihedral angle ranging between 0-180 degrees with 10 degrees step. We saw that static polarizability and anisotropic polarizability are affected less than static hyperpolarizability from variation of dihedral angle. The calculated torsional barrier, equilibrium dihedral angle and molecular dipole moment results from these molecules for biphenyl, phenylpyridine and phenylpyrimidine were compared with available experimental and other results determining from different computational methods.

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LASING IN DYE-DOPED NEMATIC LIQUID CRYSTAL AND PROBLEMS OF FREQUENCY TUNING BY APPLYING AN ELECTRIC FIELD IN THIS LASER

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Last years the researches of the dynamic distributed feedback (DFB) lasers on the dye doped liquid crystals was performed [1,2]. For such lasers the actual problem of the oscillation frequency tuning can be resolved at the expense of change of the bulk refractive index nematic under operating of an external electrical field.

However implementation of such DFB- laser on the basis of impurity nematic liquid crystals (NLC), in compare to the chiral nematic lasers with a static DFB [3], is integrated to the solution of a number of technological problems, associated with the necessity of reorientation of the director impurity NLC, input - output of pumping-oscillation beams without appreciable losses through the transparent electrodes obtaining of maximum amplification under limited dye concentration.

Therefore, contents of the given activity became the selection of DFB- laser optical scheme and the founding a laser dye permitting to provide reorientation in a constant electrical field at minimum electroconductivity of a layer responsible for the its photodegradation. The complexity of this problem is, that in thin (up to 100 microns) layers NLC, in which one the macroscopic orientation still is reached, the oscillation threshold of the DFB laser gets higher because of decreasing length interaction of two coupled waves in periodic structure [4], so at the expense of a decrease of amplification confined to extreme possible dye concentration.

In activity threshold and spectral characteristics of lasing dyes in NLC at excitation by second harmonics of a neodymium Q-spoiled laser for two versions of the optical schemes of pumping were studied .

The numerical evaluations of a oscillation frequency tuning of DFB-laser from an average index refraction of liquid crystals along an axis of wave propagation demonstrate a principal capability of frequency tuning in such laser within the limits of all half-width of a dye fluorescence spectrum band.

In consecrate with listed problems the spectroscopic characteristics

(absorption, fluorescence, quantum yield) number of pyrrolemethane dyes in NLC were studied. On dyed NLC with a high photon yield of a dye (98 %) the lasing is obtained: in a radiation spectrum at definite pitch angles of pumping the narrow line on a background of a band of a superluminescence is observed. The estimation of the spatial period of a arising dynamic grating, indicates a capability of oscillation in such conditions owing to a distributed feedback. The threshold, spectral and spatial characteristics of the oscillation are studied depending on excitation angle and the optical density of dye.

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CONTROL OF THE DIFFRACTION EFFICIENCY OF DYNAMIC HOLOGRAMS IN DOPED LIQUID-CRYSTAL ELEMENTS

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A keen interest shown by the researchers in activated liquid crystals (LC) is due to great potentialities of their use in the developed controlled LC-structures intended for spatial-temporal modulation of laser radiation, processing and imaging of optical information.

The present work is an experimental study into anisotropy of the diffraction efficiency of dynamic holograms formed on four-wave phase conjugation in the oriented layer of a dye-activated nematic liquid crystal. The schemes for the electrically-controlled diffraction elements on the basis of activated LC media are proposed.

The technique of doping a nematic liquid crystal with a dye to create components having the electrically-controlled orientation of the dye molecules is optimized. An external electric field enables one to control optical thickness of the doping dye in LC by variations in the LC director orientation.

The relationship between the optical thickness of a medium or diffraction

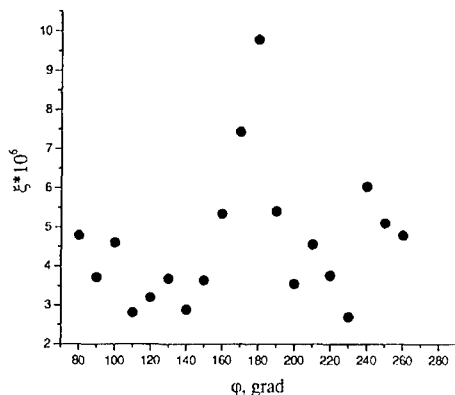


Fig. Diffraction efficiency of dynamic holograms as a function of the LC director orientation angle (dipole moment of dye molecules) with respect to the incident-radiation polarization vector for LC cells $100 \mu\text{m}$.

efficiency of the recorded holograms on the LC director orientation angle (dipole moment of dye molecules) with respect to polarization of the incident radiation is examined experimentally. Dynamic holograms are recorded using the second harmonic radiation of an yttrium-aluminum garnet laser with a pulse length of 20 ns.

It is shown that replacement of the perpendicular orientation of LC molecules relative to the radiation polarization vector by the parallel one results in the optical density of the medium increased by a factor of 1.5, that conforms to a triple change in the diffraction efficiency of dynamic holograms

recorded on four-wave interaction (see Figure below).

THIRD HARMONIC GENERATION IN DIFFERENT CYANINE DYES IMMOBILISED IN POLYMER MATRIX BY MONOLAYER SELF-ASSEMBLY TECHNIQUE

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We investigated the third harmonic generation (THG) efficiency in J-aggregates of different cyanine organic dyes immobilised in polydiallyldimethylammonium chloride (DADMAC) matrix by monolayer self-assembly technique. Molecules of all dyes are similar to that studied in [1]. Molecules of Dyes I and II are noncentrosymmetric. In the Dye I one of the benzene aromatic group (the nearest to the center of molecule) is substituted for the pyrrol group with CH_2 side group. In the Dye II one of the end benzene groups is substituted for thiophene group. The molecule of the Dye III is centrosymmetric with phenyl groups in place of benzene groups on both ends of the molecule.

In experiments, radiation from LiF:F^{2+} laser ($\lambda=1230\text{nm}$, total pulse energy $E=0.2\text{mJ}$, $\tau=10\text{ ns}$, $f=10\text{ Hz}$) focused on the sample (the spot diameter $d=0.01\text{mm}$). The maximum of third-harmonic generation was detected at a 415nm . Wavelengths of all interacting waves were out of absorption region for each dye. We compared the radiation conversion signal obtained from our polymer films with that obtained from fused quartz. The third-order optical susceptibilities χ divided by that value for quartz are described in the Table (measuring error is 15%). Here, λ_M and λ_J are wavelengths (in nanometers) of maximums in absorption spectra for monomers and J-aggregates, D is a film optical density on the wavelength λ_J .

Dye	χ	D	λ_M	λ_J
I	8	2.5	596	688
II	19	3.25	580	660
III	9.5	1.6	507	545

We measured THG efficiency dependency for different number of Dye II/polymer layers. We find out that this value depends on the film optical density (and on number of layers) linearly.

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SIZE DEPENDENCE OF THIRD-ORDER NONLINEAR OPTICAL RESPONSE PbS NANOCRYSTALS IN PVA

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A new polymer composite based upon poly(vinyl alcohol)-PVA containing nano-particles of PbS has been created. PbS concentration in polymer composite is about 4 vol%. To obtain particles of different sizes a colloidal solution of PbS in PVA has been heated at 70 °C up to 72 hours.

Using X-ray diffraction peaks widening we have determined that the mean size of a PbS particle is 9 nm (heating 12 hours), 14 nm (heating 48 hours), 18 nm (heating 72 hours). According to the hyperbolic zone model [1] the band gap E_g of PbS semiconductor particles in our polymer composite is 0.73eV (9 nm), 0.56 eV(14 nm) and according [2] 0.41eV(18 nm).

Nonlinear refraction of our samples with the thickness of 3 μm to 30 μm has been studied in the scheme of the degenerate four wave mixing.

A frequency doubled YAG:Nd³⁺ laser ($\tau_p=20\text{ns}$, $\lambda=1.064\mu\text{m}$) was used as a source of radiation. Reading out of the dynamic holographic gratings recorded in the material was carried out by means of CW He-Ne laser. Our materials was shown to exhibit third-order nonlinear response characterized by the optical nonlinear susceptibility $\chi^{(3)}(\omega;\omega,-\omega,\omega)$. The value of the susceptibility was calculated using diffraction efficiency of the recording gratings. We have obtained a value of $\chi^{(3)}=(2.18\pm0.56)\cdot10^{-16} \text{ m}^2/\text{V}^2$ (9nm); $\chi^{(3)}=(6.25\pm1.75)\cdot10^{-16} \text{ m}^2/\text{V}^2$ (14nm); $\chi^{(3)}=(6.54\pm2.29)\cdot10^{-16} \text{ m}^2/\text{V}^2$ (18nm); which is higher than that of both known non-organic optical nonlinear materials and other composites containing nano-particles of other origin under infrared pumped. Nonlinear refraction time response of our composite was measured to be not longer then 20 ns.

The experimental technique used in our studies made it possible to register optical nonlinear response caused by fast electronic mechanisms. Since the PbS nanocrystal size (9 nm) is a factor two less then the exciton diameter in bulk PbS (18 nm) so the electronic mechanism of nonlinear refraction in our material could be connected with the strong spatial limitation of the charge carriers. This factor may be a reason for the observed large third order optical nonlinear susceptibility $\chi^{(3)}$ [3].

The material under study is perspective for optical data processing.

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TRANSIENT PHOTOINDUCED REFRACTIVE INDEX VARIATIONS IN DYE-DOPED NEMATIC LIQUID CRYSTAL CELLS

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Liquid crystals (LC) are well known as prospective materials for optical devices because of their giant nonlinear optical (NLO) response [1]. In particular, orientations of molecules in LC samples may be changed by illumination with polarized light. It was discovered [2] that a system consisting of nematic LC doped with a small amount (~1%) of organic dye exposed to intense light exhibits a reorientational response monitored via optical phase changes about two orders higher than pure LC (the phenomenon is often referred to as Janossy effect).

The kinetics of photoinduced refractive index variations in dye-doped nematic liquid crystal cells was investigated with pump-probe techniques. Second harmonic of Nd³⁺:YAG laser ($\lambda = 532$ nm) was used with 5 ns pulse duration as excitation source. Light induced refractive index changes were monitored within cw He-Ne laser beam ($\lambda = 632.8$ nm) in Mach-Zehnder interferometer [3]. The kinetics of interference fringes shift were recorded with digital storage oscilloscope in the time scale from μ s to ms. Anthraquinone (AQ) dye was used as a dopant with weight concentration from 0 to 1.4%. The AQ is known as an agent enhancing the light-induced reorientation efficiency in LC. Cells with homeotropic and planar (in parallel and perpendicular configuration to laser light polarization) alignment of LC were investigated.

The refractive index variation transients are described by exponential growth/decay functions with two characteristic time constants in growth and decay, respectively. The sign of the refractive index variation depends on the angle between the director in LC and the polarization plane of the laser beam, being positive for homeotropic and planar perpendicular and negative one for planar parallel configuration. The amplitude of the effect linearly grows with dye concentration in both cases, whereas the time parameters remain constant over a

wide concentration range. Applied AC voltage in a planar parallel LC cell changes the refractive index response of LC according to permanent director reorientation thus the angle between the director and laser polarization.

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INTERMOLECULAR INTERACTION IN DYE-DOPED NEMATIC LIQUID CRYSTAL STUDIED WITH PHOTOLUMINESCENT RESPONSE

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Spectral properties of the nematic liquid crystal (LC) 5CB doped with anthraquinone (AQ) dye have been investigated. For the first time we have observed PL peak of AQ solution in LC 5CB, toluene and ethanol at 724 nm. Our experiments provide information about the path for the energy transfer between the host and guest molecules in the 5CB–AQ system, resulting in creation of a long lived excited state of the dye molecule.

PL spectrum of pure 5CB exhibits an intensive band with a maximum at about 410 nm. This band is effectively quenched by AQ molecules in the dye-doped mixed systems; a decrease of the intensity of the 410 nm band is accompanied by appearance of a new band peaking at 724 nm whose intensity increases with AQ concentration. The presence of the dye manifests itself in the appearance of an additional band in the PL excitation spectrum peaking at ca. 417 nm; this wavelength corresponds to a peak appearing in the AQ absorption spectrum and is close to the maximum of the main PL band of 5CB. The spectral overlap between the 5CB emission band and AQ absorption band creates favorable conditions for an effective excitation transfer from the LC matrix to the dopant, reflected in the effective quenching of the emission from 5CB.

The lifetimes of the excited species have been estimated using time-resolved PL technique. The upper limit of the lifetime of the S_1 state of 5CB dimer is of the order of nanoseconds, in agreement with literature. Additionally, our experiments

revealed the existence of a state having approximately the same energy and emitting in the millisecond range, whose origin remains to be explained.

In the mixed systems, energy of the S_1 state of the 5CB dimer is effectively transferred to the (non-emitting) S_m state of the dye molecule. The transfer is very efficient due to an almost complete overlap of the emission spectrum of the matrix and the absorption spectrum of the dye in the 417 nm range. Finally, the T_1 state of AQ is populated via an intersystem crossing. The lifetime of the T_1 excited state is of the order of few milliseconds.

The long-term relaxation creates condition for the charge delocalization and molecular polarizability increasing. The strong interactions and slow excited state relaxation time can explain the origin of the anomalous influence of AQ dopant in the Janossy effect.

POLYMERS AND POLYCOMPLEXES OF AZOBENZENE WITH COBALT FOR HOLOGRAPHIC AND ELECTROOPTICAL MEDIUMS

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Novel polycomplexes (PC) 4-methacryol-(4'-carboxy-3'-oxy)azobenzene with cobalt (C1) and 4-methacryol-(4'-carboxy-3'-oxy)-azobenzene with cobalt (C2) are synthesized for the first time. Kinetics of recording and relaxation of a plane wavefront hologram ($\lambda = 532$ nm, 100mW), thermal dependence of birefringence, absorption spectrum before and during application of external electric field, dependencies photoconductivity and electric conductivity on light irradiation time and external electric field strength were investigated in films of these PCs. Time constants of formation and relaxation of holograms make up minutes and are higher for C2 than for C1. Birefringence effect rising for low temperatures (within the range 4.2 – 300 K) testifies that polarization hologram is recorded. Influence of external electric field on transmission of polarized light through the films were detected. Mechanism of the electrooptical effect in samples preliminarily irradiated with linearly polarized light is guided by appearance and

accumulation of photoinduced dipole moments of azobenzene groups isomers that are responsible for formation of holographic diffraction grating as well.

The maximal influence of external electric field is observed within the visible range at the long-wave absorption edge of azobenzene groups. In the external electric field the photoinduced dipole moments change their orientation respectively to the electric vector of incident light wave providing changes of optical anisotropy of the investigated films. In the PCs without metallic ions external electric field lead to alignment of the photoinduced dipoles along the force lines and as a result interaction between these dipoles and polarized light decreases. In the PC films with cobalt ions polarized light is more scattered and depolarized in the external electric field. This fact can be attributed to more effective interaction between Co^{2+} and electric field than between the dipoles and the field. Whereas the ions are bound to isomers of azobenzene groups, the direction of the connection does not coincide with the direction of photoinduced dipole moment. Therefore, change of orientation of the photoinduced dipoles in the external electric field while connection with metallic ions is present can be opposite the changes in PC without ions. Phenomenological model qualitatively explaining experimental results is proposed.

INFLUENCE OF POLYMER MATRIX ON THE SENSITIVITY OF THE HOLOGRAPHIC RECORDING MEDIUMS WITH ORGANIC DYES

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The holographic registration mediums (HRM) based on carbazol, naphthalene, anthracene, fluorene coolygomers was obtained. In this systems the intraionic organic dyes were used as the centers of light absorption and charge carriers photogeneration. It was investigated optical, electroconductive and photoconductive properties of these polymers films. Besides, there were observed the informational characteristics of HRM. These measurements are executed by the photothermoplastic method registration of holograms by using He-Ne laser ($\lambda=633$ nm). The measurements were realized by registration the holograms of the

plane wave-front with intensity relationship of light beams – 1:1. The controlled parameter of this process was efficiency of diffraction measured in the dependence of exposition (dose of irradiation) at hologram registration process. At the constant concentration of the dye (1 mass %) the greatest holographic sensitivity was attained in a case of naphthyl- and anthracenyl- containing coolygomers. The increase of holographic sensitivity is correlated with the increase of the photoconductivity current density at the small change of the dark-conductivity in the sandwich-structure samples of these films and at electrical contacts of Ag, $\text{SnO}_2:\text{In}_2\text{O}_3$. The latter is evidence of the increase of charge carriers generation efficiency and the improvement of their transport conditions in the external electrical field.

EFFECT OF POLYMETRINE CHAINE LENGTH OF MEROCYANINE DYES ON SENSITIVITY OF HOLOGRAPHIC RECORDING MEDIA

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The film holographic recording media (HRM) based on photoconducting polymers (PP), in which as of light absorption centres and photogeneration centres of charge carriers used merocyanine dyes (MC) of the common formula $\text{D}-(\text{CH}=\text{CH})_n-\text{A}$ with the strong donor D and acceptor A, are created. The optical, conducting and photoconducting properties of PP+1mas. of % MC films are researched. The information characteristics of HRM based on these films (width 1-1.1 ms) are measured by the photothermoplastic way of the holograms recording at the use of He-Ne laser ($\lambda = 633 \text{ nm}$). With the lengthening of a polymethine chain (increase n) the absorption band undergoes the bathochromic shift and captures near IR range. With an increase n the electroconductivity current density is incremented; the photoconductivity current density and the holographic sensitivity of HRM decreases.

The electroconductivity current density and the photoconductivity of polymer films are measured in samples of sandwich - structures with contacts Ag and $\text{SnO}_2:\text{In}_2\text{O}_3$. The information characteristics are defined at the holograms recording of a plane wavefront with a relation of light rays intensities 1:1. The inspected parameter was diffraction efficiency. It is measured depending on an exposure (radiation dose) at the holograms recording. The decrease of holographic

sensitivity of MC is connected to propagation n with an increase of donor and acceptor ability of the end groups D and A of a dye molecule. Herewith the electroconductivity of polymer films is incremented at the expense of amplification thermogeneration of holes, owing to shift of absorption spectra in near IR range, and the photoconductivity decreases because of an decrease of the energies difference between HOMO of MC and PP. It was exhibited that the holographic and spectral sensitivity of MC can regularly be operated by the variation D, A and n .

MICROFABRICATION OF PHOTONIC STRUCTURES IN AZOPOLYMER FILMS

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There are many ways of making periodic nano- and microsize structures in polymers. A well known method for writing periodic structures uses interference of two crossed laser beams [1,2]. The main limitation of this method is a periodicity of the gratings.

There is a possibility to write microsize patterns using a single laser beam only by tightly focusing it on thin azopolymer films and moving the support. This method allows to fabricate any periodic and nonperiodic microstructures. Examples of such structures like directional coupler and Mach-Zehnder waveguide interferometer were inscribed and will be presented. To write patterns using a single beam the sample needs to be placed on x,y,z-nanopositioning stage. Stage was able to move 20 μm range in three dimensions. A microscope objective ($\times 100$), which focuses laser beam in to a diffraction limited spot, was located between the laser and the sample. We used He-Ne laser line ($\lambda = 543.5 \text{ nm}$) which gave spot size near to 1 μm . Piezo-stage was controlled by written by us computer program to create desired two dimensional micropatterns on the azopolymer films. The third direction allowed us to set the sample directly in the lens focal point. All patterns were quite easy observed through a polarization microscope due to light induced birefringence.

This single step photofabrication technique allows for the production of

various diffractive optical elements as well as light guiding structures with complex surface profiles for photonic uses.

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LESSER-KNOWN APPLICATIONS OF PIEZOELECTRIC AND PYROELECTRIC POLYMERS

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The piezoelectric effect was first observed in polyvinylidene fluoride polymer (PVDF) in 1969 and the pyroelectric effect was found several years later. A number of additional ferroelectric polymers have been discovered since that time including the copolymer PVDF with trifluoroethylene (P(VDF-TrFE)), and the odd-numbered nylons. A large number of applications of piezoelectricity and pyroelectricity have been developed. The magnitudes of the effects in polymers are much lower than those of ferroelectric ceramics (an exception is the piezoelectric effect in porous polymers). However, other factors make these very desirable materials for applications. The polymers have low permittivities, low acoustic impedances and low thermal conductivities. They are available in large area sheets and they are flexible and relatively low in cost. Major applications include microphones and loudspeakers, ultrasonic devices, SAW transducers, actuators, infrared detectors and many others. This review will describe some of the lesser-known applications of these materials in the areas of tactile devices, energy conversion, porous polymers, property measurement, pyroelectric infrared sensors, shock sensors and space science.

ELECTRONIC PROPERTIES OF ORGANIC SEMICONDUCTORS BASED ON NONCONJUGATED POLYMERS

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The paper presented a review of experimental results on the charge transport study in the polymer materials, possessed charge instability. The base of these materials is nonconjugated polyaromatic compounds. Characteristic feature these materials is a wide of band gap up to 4.3 eV and the value of first ionization potential about 6 eV. Electronic energetic parameters like these are typical for insulator materials. However it was established that there are not only hopping mechanism of charge transport possible but coherent too in such organic systems. Wide band gap organic material capable to transport charge carrier effectively under certain conditions and the same time conductivity can reach 10^5 (Ohm·cm)⁻¹ value and current density up to 10^6 A/cm² and more. Transformation to conducting phase may occur with different fields and influences, such as electric field, magnet field, pressure, temperature and others. These transformations are reversible as a rule. There is three main of the phenomena fields may be emphasize: electro-optical, switching, and electronic phenomena, including nanophenomena. Electro-optical phenomena are electroluminescence first of all [1]. Switching phenomena unites as following switching induced by electric field [2], pressure [3], magnet field [4], boundary condition changing [5], traps thermoionization [6], particle irradiation [7]. Electronic phenomena which can observe in thin polyarylide films are as follow electron cold emission [8], superconductivity [9], charged induced nanomemory [10], quantum dot generation [11].

The common point of view on high conductivity mechanism in wide band polymer is absent now. In [12], for example, have suggested a possibility of narrow band forming in the middle of band gap. This band appears as a result of specific interaction between charge and molecules. That narrow band posses to explain a lot of experimental data. For example, a small value of external influences, inducing an abnormally high changing in electronic properties of organic materials; high sensitivity of polymer film conductivity to changing of boundary conditions on the metal-polymer interface, injection giant magneto resistance in ferromagnetic-polymer structure and many others.

The paper has discussed the possible applied direction of new electronic phenomena. Partially, creating nanostructures of multi level information recording based on quantum dimensional phenomena, inducing by external influences, different nano- and space- distribution sensors, spin valves and filters, metal free organic adhesives with high anisotropic conductivity and others.

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CONJUGATED POLYMER CHARGE-TRANSFER COMPLEXES: A WAY TO LOW-BANDGAP PHOTONIC MATERIALS

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As is well known for small aromatic conjugated molecules, they can easily form intermolecular charge-transfer complexes (CTC) in the electronic ground state with a molecule having higher electron affinity. CTCs usually have characteristic optical absorption in the optical gap of both the donor and acceptor¹. This property of CTCs might be used for extending the photosensitivity of photonic materials into the red and near-IR spectral range. In particular, it is important for polymer solar cells to extend their sensitivity in the red range to match the solar spectrum².

Although blends of conjugated polymers with various organic acceptors usually do not show any signatures of ground-state CT interaction, we have recently found that a ground-state CTC is formed in donor-acceptor blends of MEH-PPV with 2,4,7-trinitrofluorenone (TNF) or 1,5-dinitroanthraquinone (DNAQ)³. Optical absorption spectra of the blended films are not-additive: a CTC band appears in the optical gap of MEH-PPV extending down to the near-IR region. Vibrational spectra of the blends also indicate the ground-state charge transfer: several vibrational donor (acceptor) bands demonstrate frequency shifts both in the Raman and the IR spectra.

We have observed that long-lived photoinduced charges can be generated in the MEH-PPV/TNF and MEH-PPV/DNAQ blends for photoexcitation either into the CTC or MEH-PPV absorption bands⁴. However, the photocurrent is quite low in these blends as compared with MEH-PPV/fullerene blends possibly due to high geminate recombination in the CTC or/and low charge mobilities of the acceptors.

To enhance the separation and collection of charges photoexcited in the CTC, we have studied ternary blends consisting of MEH-PPV, TNF or DNAQ, and C₆₀. Using photoinduced absorption spectroscopy, we have found that the photoinduced charge transfer from the photoexcited CTC to C₆₀ is highly effective in MEH-PPV/DNAQ/C₆₀ blends and is ineffective in MEH-PPV/TNF/C₆₀ blends. Therefore, tuning the difference between the LUMOs of the acceptor forming the CTC and fullerene, one can achieve effective generation of long-lived charges in ternary blends. We discuss how a polymer CTC could be used as a red absorber in polymer/fullerene solar cells.

One of the basic drawbacks of conjugated polymers is their poor photooxidation stability in ambient conditions. We have found that the photooxidation rate of MEH-PPV in the blend with TNF under visible irradiation can be a few orders lower than that of pristine MEH-PPV. Our findings suggest that a PPV-type polymer in a donor-acceptor blend could have the lifetime reaching thousands of hours under visible radiation of solar intensity in ambient conditions without encapsulation.

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NEW PHOTOVOLTAIC COMPOSITE MATERIALS BASED ON NITROGEN CONTAINING FULLERENE DERIVATIVES

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Synthesis of new materials for photovoltaic (PV) devices based on composites of conjugated polymers and fullerene derivatives are intensively investigated nowadays [1-3]. In this type of materials the effective interaction between a conjugated polymer acting as a donor and [60]fullerene or its derivative acting as an electron acceptor takes place in the entire volume forming bulk-heterojunction. Highly soluble fullerene derivatives are needed to produce such (PV) devices: an example is MEH-PPV/PCBM composite [3]. We synthesized new soluble nitrogen containing mono-, tetra fullerene adducts by the reaction of organic azides and amines with the [60]fullerene:

- (1) 2-azahomofullereno-5- nitropyrimidine - $C_{60}N-(C_4N_2H_2)-NO_2$;
- (2) 2-azahomofullereno-dipropyl isocyanurate pentyl - $C_{60}N-C_3H_{10}-(C_3N_3O_3(C_3H_5)_2)$;
- (3) 2-azahomofullereno-O,O-dibutylphosphate - $C_{60}N-PO(C_4H_9O)_2$;
- (4) tetrakis(benzilamine)octahydro[60]fullerene - $C_{60}H_4[NH(CH_2-C_6H_5)]_4$.

The structure of the adducts was studied by ^{13}C NMR-, UV-, IR-spectroscopy and cyclic voltammetry. The synthesized fullerene derivatives 1-4 are better electron acceptors than C_{60} and PCBM (its potential is 0.09 V more negative than that of C_{60}). The comparative investigations of the IR- and optical absorption spectra of blends MEH-PPV/fullerene derivative in solution and in film showed no ground-state interactions between the components. Photoluminescence experiments, current-voltage measurements were performed on prototypes of PV cells based on MEH-PPV and blends MEH-PPV/fullerene derivative to investigate the charge transfer process. Microstructure – properties correlation of blends polymer/fullerene were investigate. We found that PL of MEH-PPV are completely quenched by a small (about 1-5% wt.) admixture of the fullerene derivative which assumes a high efficiency of charge separation in the composite material. The external quantum efficiency (EQE) of the PV device containing fullerene derivative (about 75% wt.) is two orders of magnitude higher than for the device based on pure MEH-PPV.

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PHOTOINDUCED CHARGES IN MEH-PPV/Pt_{0.75}C₆₀ DONOR-ACCEPTOR COMPOSITES

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Fullerenes and their derivatives in blends with conjugated polymers are well known to be the most effective acceptors in photoinduced charge transfer reaction. In addition, fullerenes in these blends can form a highly conductive network for collection of photoinduced charges that makes fullerenes indispensable in polymer solar cells. However, the active layer of such an optimized cell contains from 45% [1] to 80% [2] of methanofullerene (PCBM) by weight, which weakly absorbs the solar light. In this work, we study a recently synthesized fullerene-based coordination oligomer (Pt_{0.75}C₆₀)_n as an acceptor for the photoinduced charge separation and charge transport in bulk heterojunction devices. We were motivated that (Pt_{0.75}C₆₀)_n chains could facilitate electron transport in the bulk heterojunction allowing decreasing the fullerene content in it. We have done comparative studies of optical and photophysical properties of MEH-PPV/Pt_{0.75}C₆₀ and MEH-PPV/C₆₀ blends by using optical absorption, photoluminescence (PL), photoinduced absorption (PIA) spectroscopies; and photoelectric methods.

(Pt_{0.75}C₆₀)_n was synthesized by reaction of C₆₀ with Pt(dba)₂ (dba= dibenzylidene-acetone) at molar ratio Pt(dba)₂/C₆₀=3/4 according to [3]. The compound was characterized by elemental analysis, IR and Raman spectroscopies.

Drop-cast and spin-cast films of MEH-PPV/Pt_{0.75}C₆₀ and MEH-PPV/C₆₀ blends were prepared from chlorobenzene for various donor-acceptor ratio. For photoelectric studies we fabricated bulk-heterojunction photodiodes according to the common procedure.

Optical absorption spectra of MEH-PPV/Pt_{0.75}C₆₀ composites are similar to those of MEH-PPV/C₆₀ indicating the absence of essential donor-acceptor interaction in the electronic ground state. We have observed that PL quenching is higher in MEH-PPV/C₆₀ blends implying more efficient charge separation. This is in accordance with our PIA spectroscopy data indicating that the MEH-PPV polaron band at 1.3 eV in MEH-PPV/C₆₀ blends is ~2 times higher compared to MEH-PPV/Pt_{0.75}C₆₀ blends. Analyzing our PIA and PL data, we show that MEH-PPV excitons in MEH-PPV/Pt_{0.75}C₆₀ blends are not completely quenched in contrast to MEH-PPV/C₆₀ blends. We discuss the following factors that could explain the observed difference in photoinduced charge transfer in MEH-PPV/Pt_{0.75}C₆₀ and MEH-PPV/C₆₀ blends: (i) lower electron affinity of (Pt_{0.75}C₆₀)_n than C₆₀ and (ii) more acute phase separation observed in MEH-PPV/Pt_{0.75}C₆₀ blends as compared with MEH-PPV/C₆₀ blends. Photocurrent excitation spectra show that efficiency of photogenerated charge collection in MEH-PPV/C₆₀ blends is also higher in contrary to our expectations. Reasons for this and I/V curves in MEH-PPV/Pt_{0.75}C₆₀ devices are discussed.

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THE FORMATION OF σ-BONDED (FULLERENE)⁻₂ DIMERS AND (Co^{III}TPP-FULLERENE)⁻ ANIONS IN IONIC COMPLEXES OF C₆₀

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Different aspects of the formation of (fullerene)⁻₂ dimers and (Co^{III}TPP-fullerene)⁻ anions in the ionic complexes of C₆₀ and C₇₀ are discussed. Those are:

- 1). The reversible two stage dimerization of C₆₀⁻ radical anions in ionic complex of C₆₀ with bis(benzene)chromium: (Cr^I(C₆H₆)₂⁺⁺)(C₆₀⁻)-C₆H₄Cl₂ (**1**).

Crystal structures of monomeric (90 K) and dimeric (250 K) phases were solved and the changes in the magnetic properties at the dimerization were discussed. It is shown that dimerization is realized within two different $C_{60}^{\bullet-}$ pairs and results in the formation two types of dimers with different stability in one complex.

2). Sterically hindered dimerization in ionic multi-component complex $\{Cr^I(C_6H_6)_2^{2+}\} \cdot \{Pd(dbdtc)_2\}_{0.5} \cdot (C_{60}^{\bullet-})$ (**2**) (dbdtc: dibenzylidithiocarbamate). Fullerene radical anions form pairs in **2** with the shortest interfullerene C...C contact of 3.102 Å indicating that $C_{60}^{\bullet-}$ can dimerize. SQUID and EPR evidence the formation of $(C_{60})_2$ dimers below 120-140 K and thier dissociation above 140-160 K.

3). The formation and properties of σ -bonded $(Co^{II}TPP \cdot C_{60}^-)$ anions in ionic multi-component complexes $(D^+)(Co^{II}TPP \cdot C_{60}^-)$, where D is $Cr^I(C_6H_6)_2^{2+}$, TDAE $^{2+}$ and other cations (**3-5**). It is shown that $C_{60}^{\bullet-}$ forms σ -bonded diamagnetic $(Co^{II}TPP \cdot C_{60}^-)$ anions with the Co...C contacts in the 2.28-3.32 Å range. Under heating above 200 K the dissociation of these anions to nonbonded $Co^{II}TPP$ and $C_{60}^{\bullet-}$ is observed in some complexes.

4). Ionic multi-component complexes $(D^+)(Co^{II}OEP \cdot C_{60}^-)$ between C_{60}^- and cobalt (II) octaethylporphyrin contain non-coordinating tetramethylphosphonium cation in **6** and coordinating cation of N-methyldiazabicyclooctane (MDABCO $^+$) in **7**. Diamagnetic σ -bonded $\{Co^{II}OEP \cdot (C_{60}^-)\}$ anions in **6** have the Co...C(C_{60}^-) distance of 2.27 Å at 100 K and are stable up to 290 K. Both MDABCO $^+$ and C_{60}^- coordinate to $Co^{II}OEP$ in **7**. In this case a noticeably longer Co...C(C_{60}^-) distance of 2.51 Å is observed at 100 K. As a result, the reversible formation of the Co-C(C_{60}^-) coordination σ -bond is realized in **7** and was accompanied by the transition from a paramagnetic to a diamagnetic state in the 50-250 K range. It was shown for the first time that the Co...C distance of about 2.51 Å is a limiting value at which the Co-C(C_{60}^-) coordination bond is formed.

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DYE/POLYMER COMPLEX AS A FUNCTIONAL COMPONENT OF SENSITIVE SYSTEM

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A novel type of sensitive system is presented whose response mechanism is based on absorption mechanism using polymer gel and amphiphilic organic dye. The complex formation of polymer gel with organic dye and its functional properties in the aqueous salt solutions is studied. The swelling behaviour of gel and the dye absorption depend on the dye concentration and charge density of polymer chains of gel. The polyelectrolyte gels in the presence of oppositely charged dyes are collapsed due to the effective absorption of dyes and complex formation.

The polymer gels with immobilized dye immersed in the salt solution show high stability. One of the interesting tasks is the study of metal ions coextraction if dye is the chelating ligand for salt ions. It was shown that metal ions penetrate inside the gel phase and the dye/metal ion complexes form within the gel.

Amphiphilic organic dyes have been observed to self-assemble into hydrogels in aqueous solution. The effect of the type of polymer and amphiphilic organic dye, its concentration and solvent polarity on the absorption and dye aggregates is analyzed. Structure and functional properties of the assembling dye/polymer complexes were in the focuses of the present research.

Effect of polyelectrolyte (polycations and polyanions) on the formation of regular nanostructures of cyanine dyes was studied. The process of aggregation of the dyes in aqueous and aqueous-organic solutions in the presence of linear polyelectrolytes was compared to that inside the polyelectrolyte gels. It was found that the fraction of aggregated dye ions is conditioned by hydrophobicity, dimensional structure (linear or cross-linked), charge density of polyelectrolyte and solvent polarity. An increase in the number of charge units of the polymer chain and in the solvent permittivity stimulates the formation of dye aggregates.

Technique of layer-by-layer assemblies by consecutively alternating adsorption of polycation and oppositely charged dye was used to get ultrathin films polymer films. It was found that ions of cyanine dye involved in layer-by-layer assembly form high orderly structure. The increase of fraction of charged monomer units in polycations results in the enhancement of the dye absorption per one layer.

Acknowledgment

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RADIATION PARTICULARITY OF ORGANIC LUMINOPHORS IN POLYMERIC FILMS

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Interest in the study of spectral and luminescent properties of organic luminophors incorporated in solid state polymeric matrices and films has increased in the last few years because of the feasibility of their use in new technologies and devices including diodes based on organic compounds, wide-format floppy displays, optical radiation converters, and microlasers.

Spectral properties of light emitting acrylic and carbazol-based thin films (0,2 - 0,8 μm) doped with organic fluorophors were examined under usual and laser excitation. Fluorescence quantum yield, Stokes' shifts, fluorescent and absorption spectra of some rhodamines, phenalemines, coumarins, pyran, -oxazol,- and oxadizol-derivatives were investigated.

Influence of an acrylic polymer structure, namely, the presence of the functional groups, capable to form hydrogen bonds with organic fluorophores, on their spectral and radiation properties is investigated.

It was shown the spectral properties and fluorescence quantum yield of rhodamine 6G and rhodamine C in acrylic films are similar to that in ethanol solutions. These compounds have a strong fluorescence in acrylic films and exhibit intensive lasing under both XeCl-laser and YAG-Nd 2-nd harmonic laser excitation in yellow - red spectral region. These dyes are promising for microlaser engineering.

Coumarine dyes exhibit bright solvatofluorochromic properties at transition from polar proton solvent of ethanol to weakly polar acrylic films. In films coumarines have much greater Stokes' shift, than in solutions that indicate on essential reorganization of molecule structure at excitation in these environments.

Among oxazol- and oxadiazol- derivatives emitting in blue region the 2-phenyl-5-biphenyl-oxadiazol shows the best results of lasing in acrylic films.

Photophysical properties of various organic molecules have been investigated in films on the basis of oligomer of polyepoxypropylcarbazol and high-molecular polyvinylcarbazol also.

It is shown, that radiation properties of organic luminophores in carbazol containing films depend on the structure of molecules and on preparation conditions of them. For some coumarins and other compounds the fluorescent quantum yields are comparable with those for ethanolic solutions.

For compounds whose absorption bands were overlapped with a carbazol radiation one, the dye fluorescence intensity amplification was observed owing to nonradiative transfer of electronic energy from excited molecules of polymer to organic molecules. This effect was investigated under usual and laser excitation.

COPOLYMERS DEXTRAN-graft-POLYACRYLAMIDE. STRUCTURE PECULIARITIES IN SOLID STATE

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Chemical modification of rigid polysaccharide, grafting with synthetic polymers has been explored as method to develop novel hybrid materials, which can be used as sorbents and flocculants in two ways: in the form of powder for incorporation in filtering systems, or directly in solution. Clearly, the copolymer microstructure will have a direct influence on the final properties. Therefore the knowledge of the molecular structure and the way and the methods of its modification should allow one to have a better control of the size of the cavities acting as sorbent sites for pollutants.

This work is focused on the study of the structure of graft copolymers Dextran-graft-Polyacrylamide (D-g-PAA) in dependence on the distance between grafts.

The copolymers D-g-PAA based on Dextran with $M_w=20000$ and $M_w=70000$ (main chain) were synthesised by radical polymerization using Ce(IV)/HNO₃ redox systems. The ratio of molar concentration of Ce(IV) to Dextran and amount of Acrylamide monomer were kept constant in the aim to obtain the copolymers with the same number of Polyacrylamide grafts of comparable length. The products of synthesis have been analyzed by NMR ¹H spectroscopy. Molecular characteristics (M_w , M_w/M_n , R_z) of D-g-PAA were obtained by using Self-exclusion chromatography, Light scattering and X-Ray diffraction.

D-g-PAA samples were characterised in the block state by Dielectric spectroscopy (in frequency range from 1 to 50 kHz, temperature range from -100 to +100 °C) and DSC (in temperature range from +25 to +250 °C). It was established that the molecular structure of D-PAA is determined by the conformational particularities of grafted PAA chains depending on the distance between grafts on the basis polysaccharide chain.

The increase in the distance between grafts reduces steric obstacles for folding flexible PAA-chains, i.e. promotes more compact packing of them.

THERMOWAVE PYROELECTRIC PROFILING OF P(VDF/TrFE) FILMS

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Polyvinylidene fluoride (PVDF), $(-\text{CH}_2-\text{CF}_2)_n$, ($n \geq 10^4$) belongs to the class of semi-crystal organic polymers and PVDF based films are important functional materials for a variety of applications including piezo- and pyroelectric devices. Electrophysical investigations of PVDF based polymer films, especially the study of their piezo- and pyroelectric properties have attracted non-decreasing interest both for fundamental research and applications.

Pyroelectric response of commercial PVDF and P(VDF/TrFE) copolymer films of Belgium, Japan, France, Russia and USA production, has been studied in a wide range of frequencies of radiation flux modulation. Investigation has been concentrated on elucidation of role of non-uniform distribution of pyroactivity through the film thickness on the peculiarities of low frequency (~ 1 kHz) pyroelectric resonance discovered earlier in commercially available PVDF copolymer films [1]. A complex nature of this phenomenon and prospects for applications required the further investigations directed on elucidation of physical mechanism and factors determined pyroelectric resonance conditions.

Registration of pyroelectric response was performed by the photothermomodulation method using measuring set developed for complete diagnostics of ferroelectric and electrophysical characteristics of polar-active materials [1]. The samples under investigation were irradiated by modulated IR flux and generated pyroelectric response amplitude U_π and phase φ_π were measured as the functions of thermal flux modulation frequency f_m in the pyroelectric current and pyroelectric voltage modes characteristic for pyrodetector operation.

The measuring system allows one to investigate the amplitude-frequency $U_\pi(f_m)$ and phase-frequency $\varphi_\pi(f_m)$ dependences in the range of modulation frequency f_m values of 1 Hz to 100 kHz. The choice of f_m permits to change the effective temperature wave penetration depth $\lambda_t = (a_t/\pi f_m)^{1/2}$ (a_t – is the thermal diffusivity) which gives the possibility to perform the under-surface thermal wave probing and obtain the information about the thickness distribution of pyroactivity (λ_t - profiling) in the range of λ_t from 0,5 to 100 μm for PVDF samples.

The main distinction of this resonance behavior is a strong correlation between electromechanical boundary conditions, namely λ_t - profile and so space charge profile in near-surface region of the film, and different sequence of resonance f_r and antiresonance f_a frequencies under probing the sides being at different signs of poling voltage. Indeed with increasing f_m we observed the several types of controllable resonance behavior such as typical sequence of resonance-antiresonance regions ($f_r < f_a$) and also inverse antiresonance-resonance

ones ($f_r > f_a$) as well as absence of resonance phenomena when λ_t - profile becomes homogeneous. Analysis of the resonance frequencies of investigated samples has proved the connection of the pyroelectric resonance with the vibration modes of bending type. The study under acoustic excitation has shown existence of acoustic resonance at the frequencies near those of pyroelectric resonance. The same type of pyroelectric resonance behavior in the range of 50-150 kHz, which can be controlled by performing appropriate polarization process, was found in thin plates of pyroactive ceramics and single crystals.

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LIGHT DEPOLARIZATION IN GLASS PLATES WITH $\text{SnO}_2\text{:In}_2\text{O}_3$ LAYERS

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$\text{SnO}_2\text{:In}_2\text{O}_3$ (ITO) layers deposited on glass or lavsan substrates are commonly used as electrodes for liquid-crystalline and electroluminescent displays, photoelectric light energy converters, photorefractive devices, for optoelectronics and holographic recording mediums. It is discovered that ITO layers may cause distortion of information field due to their depolarizing properties. ITO layers prepared by magnetron deposition or thermal evaporation methods were used for investigations. Results obtained for different samples were very similar. Influence of temperature on transmission of unpolarized light through investigated samples with ITO layers is not registered. On the contrary, while using laser irradiation or light source with a polarizer significant change of intensity of light passed through a sample and another polarizer (analyzer) is observed. This change correspond to effect of decreasing degree of polarization in samples with ITO. The effect is observed within the whole visible light range and within temperature range $T=293\text{-}400$ K. The change of polarization degree has reversible behavior and relaxation of polarization degree after switching samples heating off occur exponentially with time constant 200-300 s that rise for samples with thick glass substrate and apparently is determined by natural heat removal from ITO layers. It is assumed that observed light depolarization effects is concerned to reversible structural changes of ITO layers occurring during temperature changes.

INFLUENCE OF EXTERNAL MAGNETIC FIELD ON PHOTOLUMINESCENCE OF POLYMETHINE DYES IN PHOTOCONDUCTING AND NONPHOTOCONDUCTING POLYMER FILMS

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The kinetics of photoluminescence intensity (I) decay of ionic and neutral of polymethine dyes in nonphotoconducting films of polyvinylethylal (PVE) and in photoconducting films of poly-N-epoxypropylcarbazole (PEPK) in a range of an external magnetic field strength ($H=0-0.5$ T) and temperature $T=113-293$ K is researched. At low temperatures in kinetics of decay $I(t)$ of a cation and neutral dyes in PEPK there is recombinational component is connected with heminal recombination of a photogenerated charging pairs. In PEPK films with an anion dye and in PVE films with all researched dyes the kinetics of decay in the millisecond range may be described by the exponential dependence $I(t) \sim I_0 \exp(-t/\tau_1)$. With an increase of temperature I decreases because of a temperature quenching of radiative transition S_1-S_0 of dye molecules (illumination wavelength $\lambda_{\text{ill}}=532$ nm). The same quenching I is observed at dyes excitation in state S_2 ($\lambda_{\text{ill}}=337$ nm). It is revealed that for the last case the dyes fluorescence is sensitive to an external magnetic field. In all researched dye-doped polymer films at high temperatures the increase H is accompanied by the decrease of I but herewith the influence of H on τ_1 was not revealed. The latter can mean that in a magnetic field the number of fluorescent dye molecules decrease, for example, because of amplification an internal singlet - triplet of conversion for transitions S_2-T_2 and S_1-T_1 . At decrease of temperature the influence H on I increases. The obtained results direct that the influence of a magnetic field on photogeneration and recombination a charging pairs in photoconducting dye-doped polymer film is caused by the operation both on spin conversion of a heminal charging pairs and on a relation of a population density of lower excited states of dye molecules, from which happens formation of the charging pairs.

PHOTOLUMINESCENCE QUENCHING STUDY OF COMPOSITES COMPRIZING NOVEL FULLERENE BASED ACCEPTORS AND MDMO-PPV

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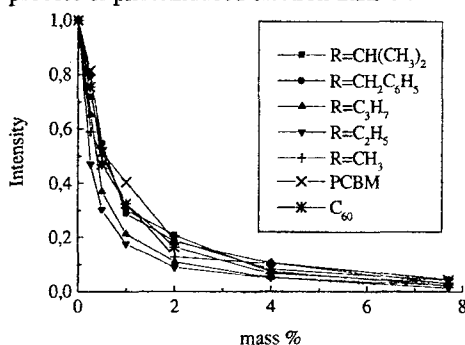
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The design and synthesis of the new materials for the organic photovoltaic (PV) cells based on composites polymer - fullerene derivatives are intensively investigated nowadays. Due to the effective photoinduced electron transfer between polymer and fullerene solar cells with high power conversion efficiency were prepared using these systems. The photoinduced electron transfer results in polymer photoluminescence quenching so such quenching is the necessary condition of the applicability of the material for fotovoltaic devices [1,2].

Poly(2-methoxy-5-(3'7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV) and methanofullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ether (PCBM) are often used as the materials for photovoltaic applications [1,2].

In this work we have synthesized some new methanofullerene derivatives of the formula [6,6]-phenyl-C₆₁-(CH₂)_n-COOR where n=2, R=C₃H₇, CH₂C₆H₅, CH(CH₃)₂, C₂H₅, CH₃ (the compound with n=3 and R=CH₃ is a well known PCBM) [3]. We have measured the dependence of polymer photoluminescence in the blends of MDMO-PPV (Aldrich) and fullerene derivatives on the concentration of fullerene in order to evaluate the ability of our compounds as the acceptors in the process of photoinduced electron transfer.



The figure shows the relative intensity of MDMO-PPV photoluminescence band at 580 nm ($\lambda_{exc}=450$ nm) vs the fullerene derivative contents in the blends with MDMO-PPV for different derivatives. Data for C₆₀ and PCBM are included for comparison.

It follows from the obtained data that the acceptor abilities of our compounds are not worse or better for some of them than for C₆₀ and PCBM.

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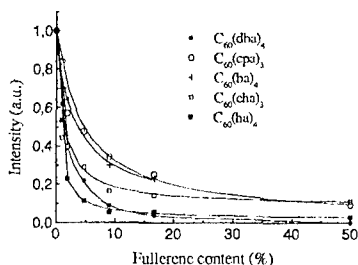
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NEW MATERIALS FOR PHOTOVOLTAIC CELLS BASED ON AMINOFULLERENES

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The design and synthesis of the new materials for the organic photovoltaic (PV) cells based on composites of a conjugated polymer and [60]fullerene or its derivatives are intensively investigated nowadays. In this type of PV devices, the effective interaction between the p-type conjugated polymer and the fullerene as n-type component can take place in the entire volume of the device ("bulk-heterojunction" cell) resulting in more efficient PV devices comparing to donor/acceptor bilayer device. Highly soluble fullerene derivatives are needed to produce such "bulk-heterojunction" cells. An example is MEH-PPV/PCBM composite (where MEH-PPV stands for poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene and PCBM is a highly soluble methanofullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester) [1]. Increasing the acceptor ability of the fullerene by chemical modification of C₆₀ can give further improvement of the device performance. From this point of view we synthesized new soluble C₆₀ derivatives with high electron acceptor ability - poly(amino)fullerenes by the reactions of organic amines with C₆₀:

(1)-tetrakis(benzylamine)octahydro-[C₆₀]fullerene, C₆₀H₄[NH(CH₂-C₆H₅)]₄, C₆₀(ba)₄;
 (2)- tetrakis(dibenzylamine)octahydro-[C₆₀]fullerene, C₆₀H₄[N(CH₂-C₆H₅)₂]₄, C₆₀(dba)₄;
 (3)- tetrakis(heptylamine)octahydro-[C₆₀]fullerene, C₆₀H₄[NH(C₇H₁₅)]₄, C₆₀(ha)₄;
 (4)- tris(cyclopentylamine)hexahydro-[C₆₀]fullerene, C₆₀H₃[NH(C₅H₉)]₃, C₆₀(cpa)₃;
 (5)-tris(cycloheptylamine)hexahydro-[C₆₀]fullerene, C₆₀H₃[NH(C₇H₁₃)]₃, C₆₀(cpa)₃
 and studied properties of the composites of MEH-PPV with these fullerene derivatives. The photoinduced electron transfer results in polymer photoluminescence quenching so such quenching is the necessary condition of the applicability of the material for photovoltaic devices [2].



We have measured the dependence of polymer photoluminescence in the blends of MEH-PPV and fullerene derivatives (1-5) on the concentration of fullerene in order to evaluate the ability of our compounds as the acceptors in the process of photoinduced electron transfer. The figure shows the relative intensity of MEH-PPV photoluminescence band at 585 nm ($\lambda_{exc}=450$ nm) vs the fullerene derivative contents in the blends with MEH-PPV for different derivatives.

We have also studied the PV properties of the mixtures of MEH-PPV with C_{60} and some of new aminofullerenes. We found that PV cells with new aminofullerenes exhibit photocurrents comparable or better than analogous cells with C_{60} .

This work was supported by RFBR (No. 05-03-33132) and PPR "Fundamental Problems of Physics and Chemistry of Nanometric-Scale Systems and Materials".

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PHOTOINDUCED PROPERTIES OF COMPOSITES OF AMORPHOUS MOLECULAR SEMICONDUCTORS WITH FULLERENE C_{60} .

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Sensabilization of many polymers of fullerene C_{60} leads to significant increase of photoinduced descriptions, in particular photogeneration of holes and electrons and their transfer in the region of transport. Such behavior of polymers, which contain a fullerene is explained by formation of covalent bonds or polymeric complexes with fullerenes, in which bond is realized due to donor-acceptor or hydrophilic-hydrophobic interactions. Particular interest is caused by modification of fullerenes of organic polymers, which contain carbazole, such as poly-N-vinylcarbazole (PVC) and poly-N-epoxypropylcarbazole (PEPC). These amorphous molecular semiconductors are important elements, used for photogeneration of holes and electrons, however they have a low photosensitivity and limited optical range. Increase of photosensitivity of these polymers together with creation of maximally large initial distance between charges by insertion of differ colorant reduces stability of photoinduced properties. Molecules of

fullerenes are the stable systems, able at complex formation, however mechanisms of their creation and transfer of charges are little studied.

A study of photovoltaic properties of composites of PVC with fullerenes C_{60} at different contents of the last is the purpose of given work. Samples were made as films, thick of which is about 100nm, which were applied on the glass undercoat with the electroconductive layer of SnO_2 at simultaneous spraying of both ingredients from separate sources at the different temperatures of a vacuum condensation.

Sharp dependence of flux density for samples, containing the different concentrations of fullerenes is observed. During a concentration higher of three gravimetric percents of C_{60} a satiation of photocurrent, caused by aggregation of fullerenes is observed. At more low concentrations, to one gravimetric percent of C_{60} , not monotonically dependence of photocurrent density takes place that is accompanied a change spectral dependence of photoluminescence. The observed dependences of photocurrent density and photoluminescence are explained of creation of complexes with the transfer of charges and a few photogeneration stages, including creation of the linked pair of electronic-holes and their dissociation on free transmitters of charge.

POLYMER FILM AS A COVER FOR PLANAR COLD CATHODES

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It was shown earlier [1] organic film might be effective cover for cold emission cathode. There are showing the availability of use of polymer coverings as emitting surfaces in later works [1,2]. In some polymers it is possible to realize the abnormal high level of conductivity without use of doping procedure. The polymers of this group are distinguished from traditional conducting polymers considerably by large width of the bandgap. In this connection, these polymers are good insulators in normal conditions. On the other hand, there are lot of works on study of electronic switching in thin polymer films. It is shown that the electronic subsystem of polymers has abnormal sensitivity to small external influences, up to switching to high-conductive condition [3].

The purpose of this paper to create planar cold cathodes with polymeric covering (thin film) and study their properties. The polished plates of silicon monocrystal were chosen as substrates. Polydiphenylenephthalide (PDP) was used as polymer covering. The experiments on registration and determination of electron emission parameters carried out in a vacuum of 10^{-5} Torr. The measuring cell were made in diode scheme with 4,7 MOhm ballast resistance.

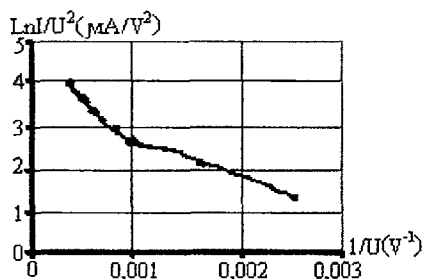


Fig. 1. Current-voltage characteristic of researched structure in Fowler-Nordheim coordinates

Usually after the first switching the emission current quickly decreases down to some stable value. That is apparently because of forming processes in a polymeric layer. Then the emission current can be supported for a long time. The minimal intensity of an electric field, at which was registered emission current, was 0,1 V/ μ .

The experimental data testify that the planar silicon cathodes with a polymer covering can serve effective sources of cold electrons. The current-voltage characteristics testify that the field electron emission take place.

Thus, as a result of our work was shown that the planar silicon - polymer structure is very perspective for application in vacuum electronic devices. First, use actually emission properties of large area flat cathodes is possible, and, secondly, technology of manufacturing of these cathodes is much easier than known analogues.

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ELECTRONICALLY ACTIVE BIFUNCTIONAL MONOMERS FOR CATIONIC PHOTOPOLYMERIZATION

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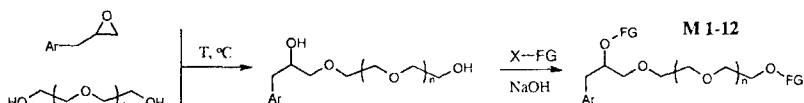
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
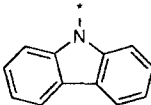



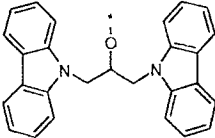

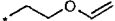
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The chemistry and technology of photo-initiated cationic polymerization is obtaining an increasing interest in scientific research and in industrial applications. The UV-curing process allows a fast radiation induced transformation of liquid systems into solid polymeric networks [1]. Carbazole monomers bearing cationically polymerisable functional groups are rapidly and efficiently polymerized by UV irradiation in the presence of onium salt photo-initiators[2]. Moreover, these monomers were observed to function as photo-sensitizers in cationic photopolymerization of clear and pigmented coatings [3].

New bifunctional carbazole based monomers containing flexible polyethylenoxide chains were synthesized by two step procedure (Scheme 1). In the first step a carbazole based oxirane was converted into dihydroxy derivative. In the second step the dihydroxy derivative was reacted with a functionalized halogen derivatives (X-FG) in basic conditions.

Scheme 1



Monomer	n	FG	Ar	
M1	3			
M2	3			
M3	3			
M4	0			
M5	1			
M6	3			
M7	0			
M8	1			
M9	3			
M10	0			
M11	1			
M12	3			

The epoxy, vinyl or oxetane bi-functional monomers were investigated for cationic UV-curable coatings characterized by different electronic and flexibility properties .

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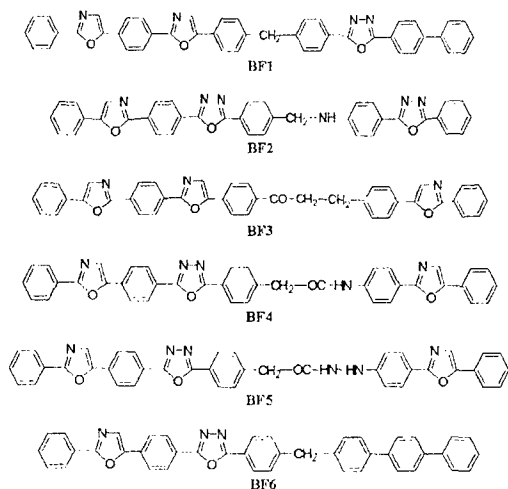
FEATURES OF THE PHOTOPHYSICAL PROCESSES IN BIFLUOROPHORE MOLECULES

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The purpose of this research work is investigation of the absorption, fluorescence and laser properties of the six bifluorophores (BFs). These molecules are objects of scientific interest since they may be used as laser-active media, energy transformers in solar batteries and as fluorescence labels. BFs are the systems with intramolecular excitation energy transfer. One moiety of a molecule conventionally is called energy acceptor (A) and other moiety is called energy donor (D).

Studied BFs consist of oxazole and oxadiazol derivatives (PPO, POPOP, PPD, POPDP), which are connected to each other in different compositions. The bridging parts in BFs are simple groups: $-\text{CH}_2-$, $-\text{NH}-$, $-\text{CO}-$ (fig.1).

The result of our investigations confirms the fact of complete intramolecular energy transfer in BFs because there is no any emission and lasing of the donor moiety of BFs. Emission and lasing of BFs belong to the acceptor moieties. By the way fluorescence and laser properties of this BFs dependent on the structure of the bridging parts and intramolecular photo-processes which take place in these BFs.



In order to understand the photo-physical processes in BFs quantum-mechanical investigations were made. The result of these studies supports the concept according to that the BF molecule has a common molecule orbital system. Photo-physical processes in this molecule may differ from acceptor molecule one.

POLYMERS GENERATED VIA DIRECTED H-BOND MEDIATED SELF ASSEMBLY

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The light scattering structural studies of polymers via H-bond mediated self assembly in solutions in organic solvents are carried out. Recently considerable studies has been made on the development of new cyanurate based (CYA-) molecules in order to combine the powerful properties of the hydrogen bonds with the proven self organisational ability of the aliphatic chains. The assemblies consist of triaminopyrimidine and cyamelide derivatives faces linked through a tartrate boloform unimers. They reveal the pronounced change in the scattering profiles versus solvent polarity at polymer weight concentrations in the very dilute regime. At higher concentration but still small 2~% the coil aggregate to built a transparent thermal physical gel which after a slow drying lead to nematic

structure The scattering profiles depend strongly on the dielectric constant of the solvent rather than their thermal behavior in term of the Flory theory of covalent polymer. These observations point to the fact that ordered polymer microstructures arise in the solutions investigated, which consist of a light phase of small assemblies which coexist with a very dilute system of swollen dynamic ribbons. A theoretical analysis of the experimental data suggests that the structure of such assemble polymers solutions can be represented by a set of randomly grafted domains consisting of ordered ribbons single or multi-twisted which may arise from stacking of fiber-like constituents. Correlations of the temperature and concentration behavior of the light scattering profiles with the dimension characteristics of the structural domains are shown.

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SYNTHESIS AND ELECTROOPTICAL PROPERTIES OF METAL-CONTAINING AZOPOLYMERS

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Monomeric and polymeric composites, hybrid systems etc. have been found to be applicable for nonlinear optics. Nevertheless polymers possess advantages over other systems due to their processability and other properties. Especially an azobenzene system [1-2] exhibits non-linear optical properties, which make it suitable for variable kinds of applications, for example as optical mediums for registration of optical holograms [3], in xerography [4] and so on.

We propose new structures of polymeric composities with changeable optical characteristics (transition and/or reflection of polarized light) under the influence of magnetic and/or electric fields.

Some new polymer metal chelates based on 4-aminosalicylic acid, 4-amino-3-hydroxybenzoic, anthranlyic and salicylic acids, phenol, 3-nitrophenol, 3-chlorophenol, N,N-diethylaminophenol with metals (Co, Ni) were synthesized.

Structure of monomers and metal complexes confirmed by data of NMR- and infrared spectroscopies.

For determination of a reactivity rating of synthesised compounds (azomonomers and its complexes of Co, Ni) and possibilities of direct polymers

syntheses in radical polymerization conditions the kinetics of their coordinative-radical polymerization (AIBN as initiator, DMF, 80°C) have been studied.

The photophysical properties of the new polycomplexes are investigated.

The effect of photoinduced electric conductivity of the polymeric films was observed.

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ELECTROCONDUCTIVITY AND PHOTOCONDUCTIVITY OF POLYMERIC COMPOSITES BASED ON ACRYLONITRILIC COPOLYMERS WITH ORGANIC DYES

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The films of polymeric composites based on copolymers (SAN) of acrylonitrile with styrene with 1% (weight) addition of anionic and (or) cationic polymethine dye were obtained. The films of pure SAN are transparent in visible and near infrared region and they haven't photoconductivity in this area. In the SAN films, which contain dye additions, the band of absorption ($\lambda_{\text{max}}=540\text{-}550$ nm) and photoluminescence ($\lambda_{\text{max}}^{\text{L}}=570\text{-}580$ nm) is determined by excitation and relaxation of excited states of dye's molecules. The increase of electroconductivity of SAN films, that contained dye additions, was detected by comparison with electroconductivity of the pure SAN films. Photoconductivity of the SAN films with anionic dye addition was detected on photoexcitation in the region of dye

absorption. Current of electro- and photoconductivity was measured in the sandwich-structure samples of polymeric films with Ag and ITO ($\text{SnO}_2:\text{In}_2\text{O}_3$) - electric contacts. The current density of electroconductivity was greater in case of negative potential of voltage on the Ag-contact.

The current density of photoconductivity (j_{PH}) dependence on value (E) of external electric field is linear in coordinates $\lg j_{\text{PH}} \div E^{1/2}$ and j_{PH} depends on intensity (I) of light of photoexcitation as $I^{1/2}$. The last is evidence of large influence of capture processes on deep traps and bimolecular recombination of charge carriers. Long exposure of the films by the light of anionic dye absorption region is accompanied by increase of electroconduction current after black-out at when $E=0$ and turning again on external electric field. The value of electroconduction current is repairing in the course of time after the end of irradiation. Photoconductivity of the SAN films with cationic dye additions wasn't found out on irradiation in visible region of light. Based on above mentioned facts it was concluded that the photoconductivity of composites (at excitation by light from dye absorption region) is caused by electron transfer from photoexcited molecules of anionic polymethine dye to accepting nitrilic groups of polymer with further transfer of electrons between nitrilic groups of SAN to the SAN. The electron transfer from the SAN to the light excited dye molecule hasn't occur in the case of cationic dye. Therefore we have concluded that the composites based on SAN with the additions of anionic polymethine dye are characterized by electronic type of conductivity.

Such polymeric composites could be studied for the purpose of creation of new electroluminescent materials.

ELECTRONIC CONDUCTIVITY OF POLYMERIC COMPOSITES IN NEAR INFRARED REGION

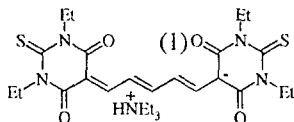
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The films of polymeric composites based on polyvinylethylale doped with small concentration of near infrared light absorbed anionic polymethine dye (1) and high concentration of organic acceptor of electrons – 2,4,5,7-tetranitro-9-fluorenone (TeNF) and (or) tetra(benzylamino)octahydrofullerene (TBAF) were obtained.



The photoconductivity of these compositions (in samples of sandwich-structures on base of such polymeric composite films with Ag- and ITO ($\text{SnO}_2:\text{In}_2\text{O}_3$)-electric contacts) was investigated. It was shown that these photoconductive composites are characterized by electronic conductivity. The photoconductivity of composites (at excitation by light from dye absorption region) is caused by electron transfer from photoexcited molecules of anionic polymethine dye to molecules of acceptor with the following electron transitions "acceptor-acceptor" between molecules of organic acceptor. It was found that the value of photocurrent increased in case of TBAF-containing composites in comparison with similar TeNF-containing ones. On the base of experimental data and fact that both type of acceptors (TBAF and TeNF) are characterized by similar values of electroaffinity we have concluded that the increasing of photocurrent value in TBAF-composites is caused by increasing of probability of electron transfer between approximately spherical molecules (TBAF) in comparison with ones with planar structures (TeNF). This conclusion was qualitatively confirmed by data of model theoretical calculations for probabilities of tunnel electron transition in solid solutions of electroaccepting molecules with spherical and planar structures.

PHOTOVOLTAIC PROPERTIES OF FULLERENE / VINYL POLYMER COMPOSITES

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Photoelectrical properties of composites consisting of fullerene molecules and different vinyl polymers have been studied.

The composites, prepared by mixing fine powdered fullerene crystallites with polymers were deposited by spin-coating method at 300K, were then placed in a cell between two glass plates coated with semitransparent ITO electrodes. The thickness of composite layers was amounted to 1-2 μm , a visual observation of the composites shows good homogeneity of the structures. We used following polymers: polyvinylcarbazole (PVK), iodine vinylcarbazole octylmetacrylate copolymer (I-VK-OMA) and polyvinylethilale (PVE).

Cells based on fullerene film deposited in high vacuum at room temperature onto glass substrates with SnO_2 or ITO transparent electrodes with thickness 0,1-0,4 microns were also prepared.

The results obtained are analyzed comparing to previous published data [1] on 5CB LC composites with C_{60} and heterostuctures (HS) of the same LC with C_{60} layer.

An increase of the photovoltage was found in all samples of polymers/ C_{60} composites comparing C_{60} film in the 2 - 3 eV range. At this region charge transfer states (CT-states) at 2,4eV and 2,7eV are present in C_{60} [2]. A sufficient increase of the intensity of CT-band at 2,4 eV is observed for the composite sample with PVK polymer, while photovoltage of composite sample based I-VK-OMA polymer rises more strongly at the region of 2,7 CT-band. Composite with neutral PVE polymer has only small rise of photovoltage in all spectral range.

Earlier we have shown [3] that band gap value of molecular crystal can be successfully estimated based on the comparison of photovoltage spectra of molecular crystal composites.

In the case of C_{60} such procedure gives band gap value 2,10-2,17 eV for different samples that is close to the value determined by a few different methods [2].

The contribution of direct CT-states excitation and their possible decay by the action of the illumination are discussed.

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NETWORKS OF POLYMER FIBRILS ENCAPSULATING MAGNETIC SELF-ASSEMBLED FILAMENTS

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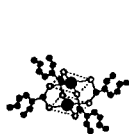
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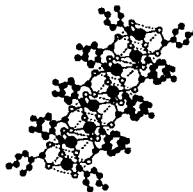
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A new type of nanomaterial prepared from ternary systems *polymer/bicopper organic complex/solvent* is presented. Each binary system displays differing types of behaviour: The *polymer solutions* produce thermoreversible gels while the *bicopper organic complex* forms randomly-dispersed, self-assembling threads in organic solvents (see figure below).



bicopper complex CuS8



filaments of CuS8

Thermoreversible gels possess a fibrillar morphology with a typical mesh size ranging from 0.1 to 1 μm . The fibrils cross-sections are usually size-polydispersed with typical diameters between 2 to 20 nm⁽¹⁾. The length of the self-assembled *bicopper organic* threads obeys a Boltzmann statistics⁽²⁾. The energy involved in the self-assembling structure is of the order of kT so that a given thread is characterized by a finite life time as scissions and recombinations constantly produce new threads. While this system may possess interesting magnetic properties, it cannot be used as such. The thread lifetime can be made infinite through encapsulation in polymer gel fibrils. It will be shown that the encapsulation can be achieved at least through two ways: *heterogeneous*

nucleation of the gel fibrils⁽³⁾ or/and solid solution formation in the gel fibrils. The formation, the structure and the magnetic properties of these materials will be discussed⁽⁴⁻⁶⁾.

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EXCITON DYNAMICS IN SEMICONDUCTING SINGLE-WALLED CARBONE NANOTUBES

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To define the origin of the electronic excited states of single-walled carbon nanotubes, femtosecond fluorescence up-conversion and frequency-resolved transient absorption measurements were used for selective excitation/probing of particular nanotubes in a micelle-dispersed preparation enriched with individual nanotubes. Analysis of the temporal and intensity profiles of the transient signals enable us to unambiguously identify the excitonic nature of elementary excitations in semiconducting nanotubes, and the predominant dynamical process as a remarkable manifestation of exciton-exciton annihilation. Our studies convincingly support the conclusion that the longest wavelength electronic excitations are of excitonic origin. A satisfactory description of the decays obtained at various excitation intensities, however, requires a time-independent annihilation rate that is valid only for extended systems with dimensionality greater than 2 in conjunction with diffusive migration of excitons. We resolved

this apparent contradiction by developing a new stochastic model, in which we assumed that the exciton states in semiconducting nanotubes are coherent, and the multiexciton manifolds are resonantly coupled with other excited states, which decay by subsequent linear relaxation due to electron-phonon coupling. The formalism derived from this model enables a qualitative description of the experimental results for the (9,5), (8,3) and (6,5) semiconducting chiral single-walled carbon nanotubes. Femtosecond transient absorption spectroscopy was also applied to map out the electronic transition energies of a selected semiconducting zigzag nanotube, the (11,0) tube.

PHOTOPHYSICS OF FULLERENE- AND NANOTUBE-DOPED ELECTROOPTICAL STRUCTURES

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Spectral, photoconductive, optical, nonlinear optical and dynamic properties [1,2] of fullerene and nanotube-doped organic conjugated electrooptical materials have been investigated to apply these structures in laser technique and information processing. The features to switch, to limit, and to modulate laser beams as well as to align and to organize human blood cells have been shown.

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CONTROL OF INTERCHAIN INTERACTION AND LUMINESCENCE OF MEH-PPV/MCM-41 NANOCOMPOSITES

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Conjugated polymers are emerging materials for electronic applications due to the tunability of their properties through variation of their chemical structure and morphology. Macroscopic properties of conjugated polymers, defined by their morphology, stipulate their luminescent properties. The efficiency of devices based on conjugated polymers could be significantly enhanced by means of corresponding control of the interchain interactions. Using of polymer-based composite materials offers an entirely new method for controlling chain conformation and thus device performance. A device based on conjugated polymer chains encapsulated in mesoporous silica would have the advantage of high carrier mobility's because all the charge conduction would be along individual chains. In this work we summarized our recent developments of preparation methods for embedding conjugated polymers inside mesoporous silica and the control of conformation and interchain interaction effects on the luminescence properties of MEH-PPV/MCM-41 nanocomposites.

New hybrid guest-host nanocomposites with variable conducting polymer loading were prepared. The preparation procedure was based on self-assembly of the organic and inorganic components via insertion of the conjugated polymer chains into the nanopores of the inorganic matrix with appropriate surface. The presence of the polymer chains within the nanopores of MCM-41 was checked by X-ray diffraction, IR spectroscopy and photoluminescence data and, according to our estimates, up to 80% of the polymer in the nanocomposites can be isolated inside the matrix. Throughout this paper, we have argued that by manipulating the nature of the polymer solvent, it is possible to change the host-guest chemistry and self-assembly of the nanocomposites and to achieve the possibility to control the extent of polymer loading and conformation of polymer chains inside the pores of the matrix due to retained memory of the initial chain conformation in the appropriate solution. Moreover this ensures higher energetics of the polymer crawling into the channels of the host and results in higher polymer loading of the inorganic matrix. We showed that confinement effect of the inorganic matrix is revealed in the PL spectra of MEH-PPV/MCM-41 composite samples as significant quenching of the band associated with aggregation of the polymer chains, as well as a red shift of the intramolecular chromophore band with respect to the spectrum of the dilute solution of the parent polymer.

The main result of this work is the development of photoresponsive hybrid organic-inorganic materials obtained by self-organization of functional organic

molecules inside the nanostructured inorganic host. Due to the highly ordered nature of these materials, these hybrids provide advantages which cannot be achieved with the single components. Control over the material characteristics, such as polymer loading, interchain interaction and chain conformation is critical for understanding their optical properties. Taken together, the results provide a prescription for the optimization of conjugated polymer film morphology for device applications.

PHOTOORIENTATION IN NEW POLYMERS CONTAINING AZOBENZENE GROUPS

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Light induced orientation of photochromic chromophores is a convenient way of creating anisotropy in polymer films. This effect can be utilized in many applications in photonics, like digital and holographic memories [1] and fabrication of optical switches [2]. We present results of optical studies of new photochromic polymer based on linear polybutadiene Krasol LBH 3000 ($M_w = 3000$ g/mol) grafted with liquid crystalline (LC) side-groups of the type 5-(4-[(octyloxy)phenyl]azo)phenoxy)pentane-1-thiol (see Fig. 1). The polymer undergoes two LC transitions during heating: From smectic B phase to smectic A at 62 °C and to isotropic phase at 98 °C.

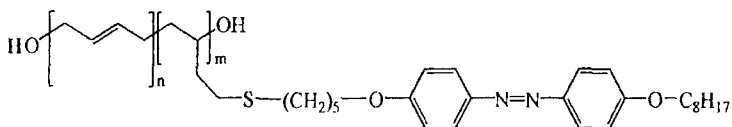


Figure 1: Chemical structure of the polymer

Azobenzene moieties of the polymer tend to aggregate in thin film, showing hypsochromic shift in optical absorption maximum of π - π^* transition, compared to their spectrum in solution. The influence of linearly polarized light of 325, 365 and 488 nm on the photoorientation process in thin film of the polymer was the

following: While the irradiation with light of 325 and 488 nm generated a stable optical anisotropy (due to the orientation of the azobenzene groups), UV light of 365 nm resulted in films with no preferred orientation of azobenzene groups. Pre-irradiation with 365 nm light and the subsequent irradiation at 325 nm led to dichroic ratio of about $R_D = 11$. Further irradiation with 365 nm erased the anisotropy again.

Light induced anisotropy was also observed in electrical conductivity of films consisting of mixture of poly(3-hexylthiophene-2,5-diyl) and the polymer under study. The electrical current anisotropy measured on the interdigital electrode structure with fingers oriented along the preferred direction of previously photooriented azobenzene moieties or perpendicular to it was observed to be one order of magnitude.

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CHIRAL ANISOTROPY OF VIBRATIONAL MODES AND RAMAN SCATTERING IN SINGLE WALLED CARBON NANOTUBES

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The thin structure of Raman spectra have been investigating experimentally in single walled carbon nanotubes (SWCNT). Theoretical calculations of forms fundamental vibrational modes SWCNT of various chiral have been carry out. It is display, that thin structure of bands in Raman spectra is determined of chiral composition and diameters of SWCNT. This dependences resolves carry out of diagnostics of composition SWCNT both from chiral and diameters in region of high frequency vibration, while in region of low frequency Raman spectra have

been relatively stabling. They contain four symmetry components E_1^+ , which is almost not dependent from chiral tubes, and which display only diameter-dependence of frequency in the whole.

Results of computer calculations of spectra of SWCNT 'ab initio', which model evolution their thin structure, is representing.

THE NANOSTRUCTURE AND RAMAN SCATTERING OF $\text{SiO}_2/\text{TiO}_2/\text{ZrO}_2$ PHOTOCATALYTIC FILMS

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The TiO_2 oxides are effective materials being used for photocatalytic transformation of ultra-violet radiation in spectral domain of their own absorption. One of the most promising directions for increasing of photocatalytic properties, improvement of thermal, chemical, and mechanical stability is a sensitizing of the nanosize titanium dioxide by doping oxides. Generally, the synthesis of composites of different oxides is implemented by the sol-gel method. However, the nature of improvement of the phototransformation in the given composites is insufficiently investigated. One of the possible assumptions of the observable influence of sensitizing by additional oxides is the formation of the solid substitutional solution on nanosize titanium dioxide particle basis and improvement of the organized state of anatase crystallite phase at long-term annealing. In the present paper the composite films $\text{SiO}_2/\text{TiO}_2/\text{ZrO}_2$ with the 70:21:9 ratios were prepared on different substrates by the sol-gel method. The films were annealed at temperature 773 K for 4 hours and at 873 K for 4, 12 and more hours before their use as photocatalysts for reduction of Cr (VI) in water environment. The changes of crystal structure were investigated by the X-ray diffraction method. Moreover, the Raman scattering was studied and the modification of vibration modes in the obtained films at annealing were determined. It is worth drawing attention that in the initial state the film is still in an amorphous phase with the topological short range ordering even after annealing at a temperature of 773 K for 4 hours. Only after increase of the annealing temperature there is a formation of a crystal phase of anatase. At this, the sizes of coherent blocks are of the order of 10 nm at the presence of essential

microdistortions. Because of abstraction of nanosize particles of dioxide titanium dioxide, doped by SiO_2 and ZrO_2 oxides the Raman scattering spectrum essentially differs from the similar spectrum of TiO_2 crystallite powder with anatase structure. However, in spite of the essential tailing, the Raman scattering bands correspond to vibration modes, which exist in the anatase phase. There are no vibration modes of other oxides in Raman scattering spectrum, what confirms the assumption of solid solution formation in composite films under the process of annealing. At the same time, the tailing of bands from high- frequency vibrations indicates the absence of stereometric component content, peculiar to titanium dioxide that is improving with the increasing of the annealing time.

COEXISTENCE OF DIFFERENT CONFORMER FORMS IN NANOSIZE POLY(DI-N-HEXYLSILANE)

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Polysilanes embedded in mesoporous glasses are a new class of composite materials,¹ with optical properties significantly different from those of bulk polymers or thin films.² New spectral features emerging when polysilanes are confined to restricted volumes³ require further investigation in order to explain electronic and optical properties of their conformational structures.

In this work the photoluminescence and luminescence excitation spectra of poly(di-*n*-hexylsilane) (PDHS) embedded in mesoporous material SBA-15 with the pore diameter of 10 nm were investigated. The measurements were carried out at various temperatures ranging from 10 K to 310 K. Significant changes in both luminescence and luminescence excitation spectra take place in this temperature range.

Luminescence and luminescence excitation spectra of the composite consist of several bands lying in the near ultraviolet region. Relative intensities of the bands vary significantly with temperature. It has been assumed that the

macromolecular chain can exhibit three different conformations in mesoporous material with nanosize pores. At least three characteristic bands were distinguished and attributed to different polymer structures: *Trans*-conformers, disordered (*gauche*) conformers and interchain aggregates. The luminescence band peaked at 356 nm and related to *Trans*-conformers dominates in luminescence spectrum below 250 K. At room temperature disordered (*gauche*) conformation and aggregate states are responsible for the bands at 340 and 372 nm respectively. When the temperature reaches 310 K, the aggregate band vanishes.

Temperature dependence of the luminescence and luminescence excitation band intensities enables us to determine absorption and luminescence spectra of all conformational structures and to obtain information about the excitation energy transfer pathways. Analysis of the data shows that different conformational structures coexist in a single nanopore.

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INFLUENCE OF SUPERMOLECULAR STRUCTURE OF POLYPROPYLENE ON PHOTOCONDUCTIVITY OF ITS COMPOSITES WITH NANOTUBES

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The light-sensitive polymers under an action of absorbed light change the structural, photo- and electro-physical descriptions, therefore are widely used for creation of environments for a record and reflection of optical information and photovoltaic elements of sun energy transformers. However they not always have

the enough high parameters of photogeneration and recombination of charge carrier, and also of their transfer in the transport region. Since a charge carrier transport in the transport region caused by them inwardly molecular diffusion and tunneling (jumps) between molecules, and efficiency of internal photoeffect depends on the width of power gap, obviously, that transformation of light energy is caused by value of intermolecular interaction and possibility of forming of donor-acceptor complexes with the transfer of charge. It is possible to expect substantial influence on formation of complexes and increase of transfer of charge in polymers at formation of their composites with chemically active carbon nanotubes, due to their geometrical features, which determine transitions of π -shells neighboring carbon atoms.

Influence of supermolecular structure of polypropylene, which appears in its composites with multiwalled carbon nanotubes at their different contents on photoconductivity, is studies in the given work. The composites samples were prepared by irrigation of polymer solution with nanotubes in dichloroethane on glass undercoat with a transparent SnO_2 electroconductive layer with a next drying at the temperature of 80°C during 1 hour. Measuring of photocurrent density was conducted at electric field voltage in the range, $(1-20) \cdot 10^7 \text{B/m}$. The crystalline structure of polypropylene-nanotubes composites was determined by a X-ray diffraction method.

The not monotonous increase of amount of crystalline component takes place, as nanotube contents increase and if a monocline phase is conserved. The block sizes of coherent dispersion increase in fibrils that indicate ability of nanotubes to create the supermolecular structure of polypropylene. Photoconductivity of composite films also has a not monotonous character. Such behavoir of photoconductivity is explained by formation in composites noticeable donor-acceptor complexes with the transfer of charge.

STRUCTURE AND ELECTRON PROCESSES IN C_{60} FILMS UNDER ELECTRON AND ION IRRADIATION

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The stable Frenkel pairs formation under the high energetic electron irradiation due to the carbon atoms displacements from the closed framework of fullerenes promotes the supplement donor-acceptor interaction between the molecules at the generation of complexes with transferred charges. Possibility of such complexes appearance and their influence on the electron processes and crystal structure in C_{60} films are insufficiently known.

In the present work the changes in fcc phase of solid C_{60} , the widths and displacements of singlet Frenkel exciton band, and also the electron transitions after the electron ($E_e=1.8$ MeV) and argon ion irradiation in glow-discharge plasma with different absorption doses are studied. The crystal structure was investigated by X-ray diffraction method, and the electron processes were studied by the photoluminescence and spectral ellipsometry methods. C_{60} films were prepared by the molecule sublimation with further vacuum condensation on the noncorrosive steel or the Si (100) substrates.

The structural fullerene fcc phase transformation changes with absorption dose increase of electron and ion irradiation. In the state of vacuum condensation there is a lot of amorphous phase and it increase with further ion irradiation due to the crystal structure destruction. The destruction isn't observed during the electron irradiation but the reflection (200) appears the intensity of which changes nonmonotonic. The (200) peak increases at the low absorption doses. It's intensity decreases when the dose achieves 100 MGy. The photoluminescence changes also differentially. The main peak with the irradiation dose increase broadens and splits due to the singlet Frenkel excitons recombination on the dimerous traps. The band gap become blurred, the interband electron transitions strips become smoothed. It is observed also for the optical conductivity spectrum. The results indicate on the appearance of complexes with transferred charges due to the irradiation. These complexes are the fullerenes with radiation defects formations. The complexes stimulate the donor-acceptor interaction between the molecules that influences on the structure and electron processes in the C_{60} films essentially.

THE PECULIARITIES OF PHOTOPOLYMERIZATION IN THE COMPOSITES "PREPOLYMER-TiO₂ NANOPARTICLES" UNDER THE ACTION OF ELECTRIC FIELD

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Per last years nanocomposite materials made of organic and inorganic components attract much attention because of technological and scientific reasons. Nanoparticles (NP) of inorganic materials introduced in host polymer medium may impact to polymer their specific electrical and optical properties [1,2].

This work is a logical continuation of our previous studies of the composites Photopolymer NOA65-TiO₂ NP [3]. It was revealed earlier that NP noticeably increase the ionic conductivity of the photopolymer NOA65. In the present work we investigate changes in the conductivity and morphology of NOA65-TiO₂ composites under the action of dc and ac electric field.

It is revealed that dc voltage, in contrast to ac voltage, initiate structural changes in the system. In an optical sense, the structure formed under dc field intensively scatters light. From the electrical point of view, dc voltage promotes an enhanced ionic conductivity in the mixture. Furthermore, TiO₂ NP in the near-cathode region change color similarly as under photo-excitation [3]. This means that titanium reduces its valency from IV to III.

The dc voltage applied during UV photopolymerization decreases ionic conductivity of final composite up to 6 times comparing with photopolymerization without the field. It seems that the redistribution of ions by electric field promotes high level of photoconversion in the mixture.

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ANALYSIS OF NANOPHASES SPATIAL DISTRIBUTION IN Au/ORGANICS COMPOSITES MANUFACTURED BY VAPOR CODEPOSITION

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Multicomponent thin film nanocomposites based on gold and organic polymers or oligomers manufactured by vapor codeposition are perspective materials for chemoresistors, SPR sensors, optical waveguides, electrooptical and nonlinear optical devices. Concentration, shape, size, anisotropy of metal nanoclusters determines the condition of plasmon resonance [1], percolation conductivity threshold, film structure stability and so on.

The purpose of present work is the investigation of metal nanophases spatial distribution in multicomponent gold/organics composites deposited by vacuum coevaporation in relation with molecular beam condensation processes. Transmission electron microscopy and optical spectroscopy allow to get supplemental data on metal clusters shape distribution.

Spatial domain Fourier and histogram analysis of TEM data gives clusters shape, orientation anisotropy, coordination anisotropy and size distributions. Nice defined lower threshold of metal nanoclusters size distribution order of few nanometres can be interpreted as critical nuclear size of film condensation processes.

Will be discussed consistency of metal concentration obtained from optical, technological and TEM analysis data. Method of molecular (or atomic) beams control at the time of composite components cocondensation in vacuum encounter difficulties with the condensation coefficients accounting. At the same time condensation coefficient of gold atomic beam on the teflon film approximately 0,5 and strongly decrease with film temperature increasing. For this reason have been investigated scattering of gold atomic beam by organic films in same conditions of composites growth. Corresponding angular diagrams data enclosed addition information on films condensation mechanism.

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STUDY OF PHOTOCONDUCTIVE AND OPTICAL LIMITING PROCESSES OF THE ORGANIC NANOSTRUCTURES

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At present time the search for materials doped with fullerenes or nanotubes is promising and effective way to apply them in information processing and laser physics. The special aspect is being made to investigate the nanostructures in the near and middle infrared. In the present paper the infrared nonlinear transmission processes in fullerene- and nanotubes-containing [1] organic systems based on polyimide and polyaniline have been considered. The futures of the structures with and without intramolecular donor-acceptor interaction have been established, as well as the solutions with nanotubes in different matrixes have been treated. The thin films, solution and dispersed liquid crystal compounds have been studied at wavelength of 633, 1047, 1080, and 1315 nm. Optical limiting properties and photoconductive peculiarities have been found. The possible limiting mechanisms have been discussed. It should be mentioned that photoconductivity of nanostructure-doped systems varies in the range of 5-6 orders of magnitude. As an additional the microscopy study has been made. The quasi-photonic organic system has been obtained (see Fig.1). Thus, the diffraction of laser beam through this structure would be considered as one of the mechanism to attenuate the laser beam.

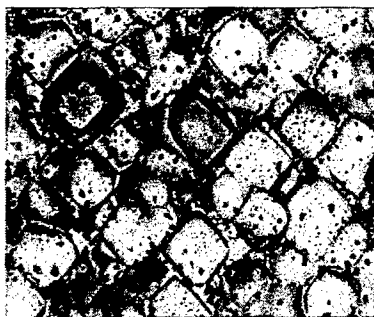


Fig.1. The general view of quasi-photonic crystals observed

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PERCOLATION PHENOMENA AND SPIN DYNAMICS IN NANOSCALE POLYANILINE – POLYMETHYLMETHACRYLATE COMPOSITES

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Polyarene conducting polymers may be considered as mesoscopic metal (a “nanometal”) with primary particles diameter near 10-20 nm [1]. This opens a possibility to create the nanoscale blends with elastic polymers by the methods of nanotechnology [2]. The mechanism of electron transport in such mesoscopic systems continues to a topic of great interest.

The electrical properties of the conducting polyaniline (PANI) blends with dielectric polymethylmethacrylate (PMMA) matrix obtained by the template synthesis [2] have been studied. It has been shown that electrical conductivity of polymer blends may be controlled in a wide range (more than 12 orders of magnitudes) by a small amount of conducting polymer. Conductivity dependence on the concentration of PANI can be explained by a percolation model with a “threshold” in the range 0,8 – 2,6 % (vol). It has been demonstrated that resistance change with temperature is characteristic for the organic semiconductors. The effective activation energy of conductivity depends on the PANI content and varies in the range $(0,26...2,16) \pm 0,04$ eV.

EPR study of the spin dynamics in PANI – PMMA composites has been carried out in the temperature interval 4,2-300 K. At low temperature the line shape becomes a Lorentzian, when temperature arising the asymmetry ratio increasing to 1,5. It has been shown that g -value for unblended PANI and PANI-PMMA composites is close to the free spin value and is constant in all temperatures. For polymer blend (10% PANI) ΔH_{pp} increases from 3,5 to 8,3 Oe in comparison with PANI and demonstrate a minimum near $T = 50$ K. The time of the spin-spin relaxation (T_2) shows a similar behavior with temperature and achieves $1,3 \cdot 10^{-8}$ s.

Based on obtained results the paramagnetic-antiferromagnetic transition about this temperature may be suggested [3].

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PHOTOELECTRONIC PROPERTIES OF NANOCOMPOSITES BASED ON POLY-1-VINYL-1,2,4-TRIAZOLE

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The chemistry nanoparticles and nano-objects, namely development of modern hybrid materials of new generation is one of priority directions of fundamental researches. The large-scale advance in development of technique, medicine, electronics, chemical technology is immediately associated to making of new hybrid materials of multifunction assignment, including composites and materials for a molecular electronics, nano-electronics, nano-medicine etc.

The studies of unusual and diversiform properties of water, different water-soluble polymeric compounds stipulated by structural features of a natural solvent are now actual.

The structured water is the basis of all alive systems in a nature and consequently the major attention is given to examination of structural features of water.

The water-soluble polymeric compounds have a wide spectrum of interesting properties and the nanoelectronics, medicine, food-processing industry are perspective in different fields of chemistry, chemical technology. Traditionally in a science about water-soluble polymeric compounds as a solvent the well-treated water (distilled or purified in traditional manner) will be utilized. At deriving polymeric solid-state systems (films, coatings) from water solutions the amorphous disordered structures are always shaped. It is proper in the majority of known water-soluble polymeric compounds.

However influence of a nature and properties of a solvent is important and key in structural examinations of water-soluble polymeric compounds. Last years the considerable successes in examination of properties of drinking water are reached. The opportunity of deriving structurally ordered or fractal water is found which has a series of unique essentially new properties distinguishing it from usual and distilled water.

Based on 1-vinyl-1,2,4-triazole is synthesized different rare-chained (co)polymeric compounds and the new materials, perspective for a molecular photoelectronics, nanoelectronics, nanomedicine are obtained on this basis.

In the work the structural features of formation of nanostructures of poly-1-vinyl-1,2,4-triazole are investigated at use as a solvent structured (fractal – dissymmetrical waters). For the first time experimentally set, that the structure of water as solvent sets structural order of a polymeric compound. From such structured polymeric compound are obtained ordered nanocomposites.

The electrical, optical and photoelectric properties of structurally ordered nanocomposites from poly-1-vinyl-1,2,4-triazole for different requirements of deriving of oriented solutions with use of structured water are explored.

The perspectives of scientific and practical examinations of nanocomposites are considered on the basis of structured water-soluble polymeric compounds of vinyltriazole series.

NANOTUBE WELDING BY ELECTRON IRRADIATION

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Now carbon nanotubes are being intensively investigated as a possible basic element of the future nanodevices. In many works e.g. [1, 2] it has been shown that electron beams are an efficient tool for properties modification of separate tubes and their complexes. Since time and spatial scales of all processes during the irradiation differ each from other on several orders of magnitude, and hundreds atoms and thousand electrons are involved in them, hence detailed simulation of these processes is very difficult. But the mean time between incoming of the beam electrons into target is the greatest. Therefore, change of properties of the above systems can be investigated within coupled rate equations describing evolution of defects and other species densities.

Within the framework of this approach the welding of nanotubes, which happens under electron beam irradiation owing to creating of new covalent bonds between walls in multiwall nanotubes, bundles, mats of nanotubes, and similar systems, has been investigated. The following processes were taken into account in electron-atom collisions: 1) excitation of atoms, 2) their ionization, 3) creating of radiation defects (at the beam energy more than 86 keV), 4) contribution of the δ -electrons. At the subsequent relaxation of the systems it was taken into account: 1) creating of new covalent bonds by the 2+2-cycloaddition mechanism, 2) quenching of the excitations in several channels, 3) recombination of the radiation defects, 4) recombination of the charges, 5) creation of structure defects different from the bonds, which were assumed only non-hexagonal rings appearing after vacancies relaxation. These processes were phenomenologically described by a system of coupled nonlinear differential first-order equations for time dependence of amounts of the new bonds, radiation defects and structure defects created within irradiated area.

It is shown, that at low radiation doses the number of the new bonds created between walls of the above systems linearly depends on the dose, and a proportionality coefficient is non-monotone depends on energy of the beam (through cross sections) and on the dominant mechanism of the relaxation (through lifetimes). When the dose increases, the number of the new bonds attains saturation, and then starts to decrease owing to accumulation of the structure defects. The experimental data (see [1, 2] and reference therein) are qualitatively coincide with the calculated curves that allowed us to improve some parameters of the model, especially the lifetimes. With these parameters the model can be used for simple analytical estimation of number of the new bonds created between nanotube walls, which is a measure of their welding, and numerical calculations of other properties of the above systems after their irradiation by the electron beams.

This work was supported by the "Dnipro" program.

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NANOMATERIALS IN TECHNOLOGY OF SECURITY PRINTING

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In technologies of security printing of documents last years the increasing application is found with the materials made with application of nanotechnologies. In particular, with use of such technologies pigments for special protective printing inks and inks for ink-jet printing are made. As an example it is possible to mention German company "Nanosolutions" which has entered the market of protective materials with luminescent nanosized pigments and inks for jet printers on their basis.

Attention of many researchers involve nanostructures on the basis of semiconductor nanocrystals type of cadmium of selenium (CdSe). Growing interest is caused as the sizes of crystals (some nanometer), and their physical properties. Unique properties of quantum dots find wide use in spectroscopy and biological researches, in particular as fluorescent labels in biological structures. Features of spectroscopic properties of nanocrystals, caused by dependence of their spectra of absorption and a luminescence on the size of nanoparticles open ample opportunities to create various composite systems and environments with new properties.

In the given work results of investigation of spectral-luminescent properties of new composite materials are submitted on the basis of heterogeneous structures

CdSe and molecules organic luminophores. Search of optimum conditions for effective energy transfer from CdSe - the donor to a molecule of organic compound - to an acceptor is carried out.

Influence of β -cyclodextrin on stabilization of spectral characteristics and photodurability of new composite environments with use CdSe and molecules of organic luminophores is offered and is investigated.

It is shown, that at research of optical characteristics of composite systems of organic luminophores with nanocrystals it is necessary to take into account the sizes of the last. At inclusion of nanocrystals different sizes it is possible to create multicenter composite materials with preset optical properties that open potential opportunities of their use in creation of unique security environments and inks.

ELECTRON PROCESSES IN C_{60} FILMS DOPED WITH METALS

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The sensibilization of fullerenes with metals influences on their electrophysical and optical properties. First of all the changes of pointed properties are the result of donor-acceptor interaction appearance during the formation of complexes with transferred charges. It is obvious that such complexes formation accompanies the changes of electron processes due to the electron structure rebuilding. The electron properties modification depends on the type of exohedral penetrated metals, their concentration and phase compound of films. These properties can change in a wide range depending on the methods of films preparing and further treatment.

In the present work the crystal structure, infilling the band gap with local impurities of metal states, interband electron transitions, location and singlet Frenkel excitons band width changes for the C_{60} films doped with titanium and copper were studied. To these investigations the X-ray diffraction, spectral ellipsometry and photoluminescence methods were used. The films were prepared at the simultaneous evaporation from two different sources of C_{60} molecules and copper or titanium atoms with further their vacuum condensation on the Si (100) substrate. The film with 100 nm thickness anneal was at 373 K during 5, 10 and 20 hours. The films had the different metal concentration that was controlled with help of different rates of evaporation.

The results showed the energetic band is blurred due to the amorphous phase predominance, and also the wide impurity zone in the band gap of C_{60} films is appeared. The bands localize and shift up to the valence band with the metal concentration increase. The exciton band corresponds the singlet excitons recombination on the dimer traps splits with an atom concentration increase but differs for the copper and titanium atoms. It is supposed the broadening is a result of excitons with transferred charges to the neighbor molecules due to the donor-acceptor interaction appearance. The anneal changes the local states in the band gap and interband highfrequency transitions. This transformation of the electron structure is caused by the increasing the crystal phase of C_{60} and its tendency to be arranged. From the other side it can be caused by the donor-acceptor interactions appeared during the process.

FUNCTIONAL HYBRID NANOCOMPOSITES FOR CATHODES OF LITHIUM BATTERIES

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Hybrid host-guest nanocomposites based on conducting polymers and layered inorganic matrices are a subject of numerous researches. The interest to these materials is conditioned by their use as functional components of electrodes in lithium batteries, emitting layers of light-emitting diodes, photovoltaic cells.

In present report, charge-discharge characteristics for prolonged cycling in the 4.0–2.0V vs Li/Li^+ potential range of hybrid materials based on vanadium oxide, particularly ternary host-guest nanocomposites, in the interlayer space of nanoparticles of the inorganic component of which there are simultaneously the macromolecules of electron-conducting polymer (polyaniline, polypyrrole, polythiophene) and ion-conducting polymer (poly(ethylene oxide)) [1-5], are presented.

The possibility of chemical (direct polymer intercalation, intercalative polymerization) and mechanochemical preparation of the hybrid nanocomposites is shown.

The effect of the preparation method and the nature of the intercalated polymer on the functional properties of the obtained materials (charge-discharge capacity, cycling, diffusion coefficient of Li^+ ions) are analyzed.

The presented data evidence the possibility of creation of hybrid nanocomposite material for cathodes of lithium (lithium-ion) batteries, which is characterized by high specific discharge capacity and stability during hundreds of cycles.

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CONDUCTIVITY OF NANOCARBON MATERIAL

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Nanocarbon material (NCM) is a complex system, which contains not only carbon nanotubes (CNT) but also amorphous carbon particles, nanographite and particles of the metal catalyst. The amount of these particles is specified by the method of NCM synthesis. The problem of the conductivity of NCM containing not only CNT of different levels of imperfection but also containing certain amounts of amorphous carbon and metal catalysts is still far from being solved. Furthermore, the main factors governing the dominant role of certain mechanisms of NCM conductivity were not precisely determined.

This paper presents the experimental studies of the resistivity of NCM of different structures and phase compositions. The main efforts were aimed at ascertaining the mechanisms of NCM conductivity with regard to their phase composition.

The NCM were synthesized by the catalytic deposition of carbon-containing gas (CO) using (Ni/Y) catalyst and has been used for the experimental studies

without further treatment. According to the manufacturer's information this material contains about 80% carbon. The electric resistivity of NCM was studied in the temperature range of (4.2-293) K using the standard four-probe technique.

The performed experimental studies allow for following conclusion: the electric conductivity of the studied NCM specimens can not be described by the single mechanism of conductivity, since none of NCM phase constituents (amorphous carbon, CNT) forms the infinite circuit. In order to describe the electric conductivity of NCM containing several phases, the serial junction model of elements with different types of conductivity according to phase content has been proposed. The calculations performed within this model showed a good agreement with the experimental results. The variations detected for the fitting parameters reflect the real variation of NCM phase composition during thermochemical treatment.

Acknowledgments

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COMPUTER SIMULATION OF INTERCALATED CARBON NANOTUBES

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The investigation of nanosized carbon clusters is of great interest due to creation of new materials in electronics, biology, chemistry, etc. Last decade saw the modelling of constituent elements and processes related to carbon cluster/intercalate systems: interaction of fullerenes and carbon nanotubes (CNT) with hydrocarbons and their derivatives, adsorption by fullerenes of different aromatic hydrocarbons, alcohols, etc. from gas and liquid phases.

The research conducted deals with the Monte Carlo simulation of the single- and double-walled CNT intercalated with different chemical elements. There has been also established the interrelation between the length of a CNT, the number and type of element atoms. The research is aimed at studying intercalated systems based on CNT and *d*-metals, such as Fe, Ni, Co and non-metal – B. Factors influencing the stability of these composites have been determined theoretically by the Monte Carlo method with the Tersoff potential.

The modelling of CNT intercalated with metals by the Monte Carlo method has proved that there is a correlation between the length of a CNT and the number of *endo*-atoms of specific type. So, in the case of a CNT (9,0) with the length of 17 bands (360 nm), unlike Ni atoms, there is observed the extrusion of a Fe atom out of the CNT, if the number of atoms in the CNT is not less than eight. Thus, this paper shows that a CNT of a certain size can be intercalated with no more than eight Fe atoms. The systems investigated are stabilized by coordination of 3d-atoms close to the CNT wall, with the radius - vector of (18-20) nm. Another characteristic feature is that, within the temperature range of (400-700) K, small systems have the stabilisation "ground" which is not peculiar of the higher ones.

The behaviour of Fe, Ni, Co and B *endo*-atoms between the walls of a double-walled CNT is explained by a dominating Van der Waals interaction between the Ni, Co and B atoms themselves, which is not true for the Fe atoms.

The obtained theoretical results were compared with available experimental data [1].

Acknowledgements

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NANOCOMPOSITES OF ULTRAHIGH-MOLECULAR WEIGHT POLYETHYLENE WITH KAOLINITE CRYSTALS

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Investigations of nanocomposites of ultrahigh-molecular weight polyethylene with kaolinite crystals were done by the EPR method using 3 cm-band radiospectrometers in the temperature range $T = 4 - 300\text{K}$. The maximum overall dimensions of plates are approximately equal to 70 nm. In kaolinite the paramagnetic impurity Fe^{3+} ions substitute the Al^{3+} ions isovalently. The iron content of kaolinite varies from 0.3 to 1.1%.

The spectrum was analysed using an EPR spectrometer with the frequency of superhigh frequency field $\nu = 9.247 \pm 0.001\text{ GHz}$ at $T = 4.2\text{ K}$. Spectrum of the impurity Fe^{3+} ion consists of two resonance lines. Line 1 for $T = 4.2\text{ K}$ is anisotropic and described by the effective g – factor $g_1 = 4.13 \pm 0.16$. Line 2 is described by the effective g -factor $g_2 = 2.15 \pm 0.1$ for $T = 4.2\text{ K}$, the line with $\Delta H_{2pp} = 0.36\text{ kOe}$.

Ion Fe^{3+} has the $3d^5$ configuration, the ground – state spin $S = 5/2$. The effective g – factor of resonance line 1 is described by the relation:

$$g = \frac{30}{7} \left\{ 1 + \frac{4}{7} \alpha (\ell_z^2 - \ell_y^2) + \frac{4}{49} (15q^2 + 4p^2)(\ell_y^2 + \ell_z^2) - \frac{2}{49} (4q^2 + 5p^2)(\ell_y^2 - \ell_z^2) - \frac{24}{343} (17q^2 + 4p^2) \right\}$$

where $q = \frac{D-3E}{D+E}$, $p = \frac{8\mu_B H}{D+E}$, $\ell_x = \sin \theta \cdot \cos \varphi$, $\ell_y = \sin \theta \cdot \sin \varphi$, $\ell_z = \cos \theta$.

Angles θ, φ define the direction of external magnetic field in the spherical coordinate system. D, E are parameters of initial splitting. D characterizes the field of axial symmetry. E characterizes the rhombic component of the field.

Analysis of experimental angular and temperature dependences and that of the effective g -factor enables us to conclude that the z -axis of each kaolinite plate

is mainly normal to extrudates axis. That is, planes of kaolinite plates are oriented mainly along the axis of extruded sample. The solid – phase extrusion arranges the kaolinite plates in ultra – high – molecular – weight polyethylene in order. The character of kaolinite plate orientation is determined by direction of deformation gradient and its value.

THE ROLE OF PHASE INTERFACE IN CHARGE CARRIER PHOTOGENERATION IN POLYMER NANOCOMPOSITES BASED ON ULTRADISPERSED MOLYBDENUM DISULFIDE

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The investigation of photoelectric characteristics for composite films based on MoS₂ ultradispersed single-layer dispersion particles [1] in *n*- or *p*-type polymer transport matrices is carried out. It is found that stabilized in *n*-matrix MoS₂ nanoparticles display efficient acceptor properties due to electron surface states. This results in the significant enhancement of photoelectric sensitivity and photogeneration quantum yield for composites of *p*-matrix with added MoS₂ acceptor nanoparticles. Just in contrast to this the large aggregated particles demonstrate rather the electron donor properties than acceptor ones.

The studying of polymer/semiconductor phase interface is carried out on bilayer heterostructures based on composite of MoS₂ particles in polyvinylalcohol (from water solution) (bottom layer) and developed transport polymer matrices (*p*-, *n*- or bipolar type) (from organic solvent) (upper transport layer (TL)). It is shown that for high MoS₂ content in bottom layer (90 and 100% wt) the interface is characterized by the broken relief and noticeable thickness. The significant role of interface with extended surface area in photogeneration of both sign carriers is found. The electron donor-acceptor properties of both MoS₂ particles and TL are of great importance. The conclusion is made that photogeneration on interface occurs upon excitation in TL absorption band as a result of photoinduced electron

transfer between MoS₂ particles and polymer TL with formation of hybrid electron-hole pair. It is found also that for the highest MoS₂ content the increase of minor carrier collection efficiency is observed due to formation of alternative transport network connected with MoS₂ particles on extended interface. The photogeneration of both sign carriers on interface evidences the availability of both acceptor and donor particles that is likely related to their wide size distribution. The photovoltaic effect is found and investigated for cells based on bilayer heterostructures with (Al,ITO) electrodes.

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ANALYSIS OF ORGANIC FIELD EFFECT TRANSISTORS AS A MAXWELL-WAGNER EFFECT ELEMENT: MEASUREMENT OF NANO-INTERFACIAL POLARIZATION AND ELECTRIC FIELD DISTRIBUTION IN ORGANIC FILM BY OPTICAL SECOND HARMONIC GENERATION

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Recent experimental studies on organic field effect transistors (FET) revealed that accumulated charges at the FET channel are mainly injected holes from Source, and they are then conveyed along the channel by the force of electric field toward Drain. This experimental findings force us to study the FET device operation from theoretical side. Maxwell-Wagner (MW) model widely employed to understand the interfacial charge accumulation at the adjacent two different dielectric materials [1] is very helpful. Without knowledge of semiconductor physics, we could derive basic current equation used to explain the FET characteristics of the field effect transistors[2]. In this study we mainly discuss on the electron transport of pentacene transistors. As holes are injected from Source as excess charges into pentacene and they are then accumulated at the interface between insulator(SiO₂) and pentacene, interfacial polarization is generated in pentacene films, and space charge field is formed. This means that the electric field in the channel changes depending on the accumulated charges at the interface. Optical Electric field induced Second-harmonic generation measurement well probes the electric field formed in the channel [3]. In this presentation, we

show how the performance of the characteristics of pentacene field effect transistors is explained based on a MW model without knowledge of the semiconductor physics, and rather with knowledge of dielectrics physics [4]. We then show how the electric field in the FET channel is modulated due to the injected holes from Source by means of DC-SHG experiment [5]. Experimental studies on some other film transistors will also be presented.

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SOLUBLE PHTHALOCYANINES: PERSPECTIVE MATERIALS FOR ELECTRONICS AND MEDICINE

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Organic and polymeric electronic devices have received increasing interest because of their potential low cost applications, easy processing and great opportunities in structural modifications of their chemical structures. Among them phthalocyanines (Pcs) play an important role as low-gap semiconducting materials. Many electrical and optical Pc applications can be mentioned, among others fuel cells, xerographic media, dynamic holographic memories, information displays, optical imaging, sensors, photodetectors and photodielectric elements.

Many electronic applications utilize the active materials in the form of thin films. Usually, Pcs are not soluble and thin films are prepared by vacuum sublimation. However, Pcs can be substituted, e.g. by sulfo-, amino- and sulfonamido-groups, and thin films prepared by wet technologies, like spin-coating, dipping, dropping and ink-jet printing. These films often retain the electronic properties mentioned above and electronic devices, as sensors, diodes, FET transistors, light emitting diodes and others, can be prepared.

Material inhomogeneity in the film thickness is critical parameter and can cause several effects, like trap formation and photovoltage generation. Polymorphism in Pcs is generally known; the crystal modification and molecular stacking influence optical and electrical properties. Electrical conductivity of Pcs is usually low, typically 10^{-14} S m⁻¹ and 10^{-8} S m⁻¹ for metal-free and copper Pc, respectively. Oxidative doping of Pc ligand with acceptors often results in highly increased conductivities, up to 10^4 S m⁻¹ (NiPc iodine complex). The one-dimensional chain of slipped π - π stacking of Pc molecules allows the formation of self-assembled molecular nanowires suitable for molecular electronic devices. The oxidation or reduction reaction often results in the change of optical spectra. Thus, in electrochemical cells a reversible electrochromism or optical switching between redox states can be developed.

Soluble phthalocyanines are also promising materials for photodynamic therapy (PDT). It will be demonstrated on hydroxyaluminium phthalocyaninesulfonates [Al(OH)Pc(SO₃Na)_n], differing in the number of sulfonate groups ($n = 1-4$). Their PDT activity during the Q-band excitation is based on the generation of triplet states, Pc radical formation and the production of singlet oxygen. Superoxide anion radicals O₂^{•-} formed simultaneously seem to be also effective in the cancer treatment. High efficiency of the cancer treatment was obtained with skin-free mice implanted with human amelonotic melanoma cancer cells (the cancer parts of testing mice were removed completely during 1 week after the PDT treatment). The phototoxic effect on bacteria cells *E. coli* was also observed.

ORGANIC ELECTROACTIVE MATERIALS FOR ELECTROPHOTOGRAPHIC PHOTORECEPTORS

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Among organic charge transport materials used in electrophotographic photoreceptors polymers and molecularly doped polymers prevail.

Molecularly doped polymers are usually understood as the solid solutions of low-molar-mass organic charge-transporting compounds (guests) in inert polymers (hosts) such as polycarbonates and polyvinylbutyral¹. The concentration of charge-transporting guests in polymer hosts usually does not exceed 50 wt. %. At

¹ P. M. Borsenberger, D. S. Weiss, "Organic Photoreceptors for Xerography", Dekker, New York 1998, 768 p.

higher concentrations crystallization of a guest can occur. The crystallization can be prevented if compounds which do not readily crystallize i.e. molecular glasses or amorphous molecular materials are used as charge-transporting guests

Organic low-molar-mass compounds with stable solid amorphous phase above room temperature are called molecular glasses or amorphous molecular materials. A real explosion of interest in organic electronically active low-molar-mass glass-forming materials occurred after the discovery of high performance multilayer electroluminescent devices prepared from vacuum-sublimed organic dye amorphous films¹.

Among organic charge transport materials used in electrophotography hole-transporting materials prevail.

In this presentation the recent results of the work on the synthesis and properties of charge-transporting polymers and molecular glasses performed in the author's laboratories are reviewed. The main attention is paid to the synthesis and studies of hole-transporting polymers and molecular glasses. In the design and synthesis of these materials aromatic amino groups have been used as the main building blocks. Charge transporting polymers have been prepared by ionic polymerization of oxiranes, oxetanes, thiiranes, vinyl ethers bearing different electroactive groups. Such polymers have been also prepared by polycondensation, polyaddition and polymer analogous reaction. Hole-transporting molecular glasses belonging to the families of condensed aromatic amines, hydrazones, enamines, ethynylenes, stilbenes and electron-transporting counterparts belonging to the families of thioxanthenes and aromatic imides have been prepared by different methods. Cross-linkable charge transport materials containing different reactive functional groups are emphasized. The thermal, optical, photophysical and photoelectrical properties of the charge transporting compounds synthesized are reported. Ionization potentials established by the electron photoemission in air technique range from 5.00 to 5.60 eV. Hole drift mobilities in the amorphous films of some hydrazones and aromatic amines reach 10^{-2} cm²/V at high electric fields as revealed by the time of flight technique.

¹ S.A. Van Slyke, C.W. Tang, U.S. Patent No. 4,539,507 (1985).

PHOTOCONDUCTIVITY IN SOLUBLE PHTHALOCYANINES

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Phthalocyanines are stable molecular semiconductors suitable for many electronic applications, like photosensors, gas sensors, transistors, solar cells, non-linear optical media, etc [1]. However, they are not soluble in usual organic solvents.

In this work we present a new group of substituted soluble phthalocyanines as potential materials for photosensitive devices. Sulpho-groups, sulphamide-groups and amino-groups were used as substituents. Zn, Cu, Ni, Fe were used as the metal core in the phthalocyanine skeleton. Optical absorption spectra consists of two strong Q and Soret bands at about 600 – 700 and 350 – 400 nm, respectively, with an enhanced broad optical window with lower linear absorption at about 500 nm. HOMO and LUMO energies of solid phthalocyanines under study are approximately 5,8 and 3,8 eV, respectively. These values depend on the character of the substituents. Acceptor-like substituents decrease these energy levels, and donor groups increase these values. Phthalocyanines under study are strongly photoconductive; the photoconductivity spectra are symbatic with optical absorption. Current-voltage characteristics show ohmic behavior at low electric fields (lower than 10^6 V m^{-1}), a strong hole injection from electrodes was observed for higher fields.

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COPOLYMERS DEXTRAN-graft-POLYACRYLAMIDE. PSEVDOPOLYELECTROLYTE EFFECT IN BINARY SOLVENTS

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Copolymers obtained by grafting polyacrylamide (PAA) onto polydextran have been synthesized by ceric-ion reduced redox initiation method. These copolymers have been characterized by light scattering, self-exclusion chromatography and viscometry and X-ray diffraction in aqueous solution. We have observed that the PAA grafted chains are significantly extended, and that the degree of 'extention' depends on the distance between grafts.

The investigations into the intrinsic viscosity of the copolymers in binary aqueous solutions water+DMF (dimethyl formamide), a "polyelectrolyte behavior" has been observed. We suspect that this effect is due to the gradual melting of a ternary complex copolymer/water/DMF upon dilution, and is foreign to any charge effect. Potentiometric titration curves obtained for distilled water and for copolymer solution were the same. We can, therefore, conclude that the degree of hydrolization of the PAA moiety in the nascent copolymer is virtually zero under the present experimental conditions.

Acknowledgements

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PHOTOPHYSICAL PROCESSES IN NOVEL 3- AND 7-SUBSTITUTED COUMARINES

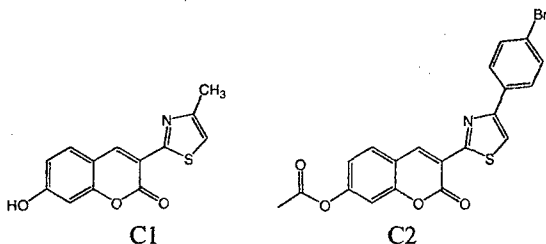
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Coumarins are used as laser dyes in the blue-green spectral range. Moreover, recently, compounds of this class have also found application in other fields of science and engineering. Thus, some benzothiazolyl-substituted

hydroxycoumarins display biological activity against gram-positive and gram-negative bacteria. There are data in the literature that these compounds exhibit anticoagulation activity and, therefore, can be used in treatment of thrombosis [1]. Many dyes of this class are used as fluorescing labels. The applications of coumarin derivatives extend further. However, despite of the wide popularity of these compounds, they remain little studied [2, 3].

In this work we studied 7-hydroxy-3-(4-methylthiazol-2-yl)-2H-chromen-2-one (C1) and 3-(4-(4-bromophenyl)-thiazol-2-yl)-2-oxo-2H-chromen-7-yl acetate (C2). The spectral-luminescent properties of coumarins were studied in DMSO.



These compounds differ by nature and position of substituents, and the differences in spectral-luminescent properties of the compounds are determined by the properties of these substituents. The strong long-wave absorption bands of both compounds located in the range of $25500\text{--}26100\text{ cm}^{-1}$. Both C1 and C2 have a strong fluorescence in range $466\text{--}480\text{ nm}$ with broad bands. The quantum yields are 0.93 and 0.53 respectively. Consequently Stokes shifts are very large (4040 cm^{-1} for C1 and 6800 cm^{-1} for C2). There is no lasing ability of the dyes.

For understanding of such behavior we have made theoretical investigations by PM3 and INDO method with spectroscopic parameterization.

Our quantum-chemical calculations show that C2 changes its geometry in S_1 -state. In the ground state the angel between *p*-Br-benzene and other molecule is 30° whereas in excited state molecule is planar. It results to large Stokes shift and broad fluorescence band. The absence of laser ability in both C₁ and C₂ we explain by strong T-T absorption from first triplet state which located in the range of fluorescence band.

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MODULATION SPECTROSCOPY AS A POWERFUL TOOL IN CHARACTERIZATION OF NOVEL OPTOELECTRONIC MATERIALS

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The major advantage of modulation techniques is that they are absorption-type techniques which together with the emission techniques like photoluminescence could give a complementary information about correlation between structural and optical properties of solids important from fundamental as well as technological point of view, where it could help to optimize the technological process. However modulation techniques give much more information than more common PL or reflectance/transmittance measurements.

This technique is not sensitive to the defect states thus its comparison with the emission spectra (Stokes shift) the recombination centers as well as nature of the recombination processes (excitonic or band-to-band recombination, energy transfer) can be determined.

Second advantage of these techniques is that they are characterized by very sharp (derivative-like) resonances which broadening, indicating the optical quality of the sample, is independent on the experimental parameters (excitation power, setup configuration) giving an information about real inhomogeneities of the energy levels. Also in case of multilayer structure it is possible to obtain signal from all parts of structure.

The most important advantage of this technique is that we can obtain information about the excited states in case of quantum confinement. This could give important information about changes in stoichiometry, stress in the sample, changes in the potential shape or quenching processes. Also from comparing this results with the simple theoretical approaches we can obtain an important technological parameters, i.e. effective masses, band off-sets, activation energies.

Another important advantage of this technique is that all presented information can be obtained at low as well as at room temperature, which is important from application point of view. Also due to so called Franz-Keldysh oscillations in the absorption spectra it is possible to obtain information about internal electric fields, and its changes from sample to sample. It is especially important issue in case of GaN transistors and other heterojunctions.

Thus modulation spectroscopy investigations of the optical properties and some physical effects, i.e. interdiffusion processes, atoms segregation processes, in quantum wells, quantum dots, quantum dashes, inorganic and organic-inorganic heterojunctions will be presented.

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POLYCYCLIC AROMATIC HYDROCARBONS AS LUMINESCENCE MARKS FOR INVESTIGATIONS OF MOLECULAR INTERACTIONS IN AUTOMOBILE PETROL

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Problem of analytical determination of oil pollutions of the environment, of analysis of composition and origin of petroleum reminders and traces is known for a long time. It is really very complicated problem and a number of methods solving this problem are based on analysis of polycyclic aromatic hydrocarbons (PAHs) in composition of petroleum products. Luminescent method of automobile petrol (AP) examination is also based on characterization of PAHs properties [1].

Steady state, time resolved and synchronous luminescence – excitation properties of different types of automobile petrol and hexane solutions of petrol were measured at room, liquid nitrogen and helium temperatures in order to study role of intermolecular interactions in formation of luminescent properties of automobile petrol. The samples for the investigation were obtained from the same oil refinery in Ukraine. We used petrol with octane numbers 76 (trade mark is A76), 92 (trade mark is A92), 95 (trade mark is A95), and 98 (trade mark is A98). Besides mentioned conditions luminescence of AP incorporated into porous SiO_2 and its dependence on keeping time was investigated too.

The spectra and decay curves of luminescence are considered as caused by emission of various polycyclic aromatic hydrocarbons (PAHs) those are components of petrol composition, which respond in various ways on transition of solutions from liquid to frozen state. It has been shown that intermolecular interactions effect on the shape of luminescence spectra, intensity of luminescence, decay kinetics of luminescence and their dependences on petrol contents in solutions. Constructed dependences of intensities of luminescence linear spectra and decay kinetics of luminescence of such PAHs as pyrene and chrysene reveal interaction between mentioned molecules. These dependences give possibility to find traces of automobile petrol in organic solvents.

The luminescence data of the liquid and frozen automobile petrol and their solutions in hexane have demonstrated in principle a possibility to investigate intermolecular interactions in such multi component systems as light oil products.

Some details of the linear luminescence spectra of frozen solutions can be used for analysis of intermolecular interaction among one type of polycyclic hydrocarbon molecules. Moreover luminescence decays and their changes caused by dilution of petrol also show the role of intermolecular interactions. Quantitative evaluation of intermolecular interactions can be performed in the future. Described results are interesting for environment monitoring and forensic examination because they reveal the possibility to determine traces of petrol and

polycyclic aromatic hydrocarbons.

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HOLE-TRANSPORTING INDOLYL-BASED LOW MOLECULAR WEIGHT AND OLIGOMERIC HYDRAZONES

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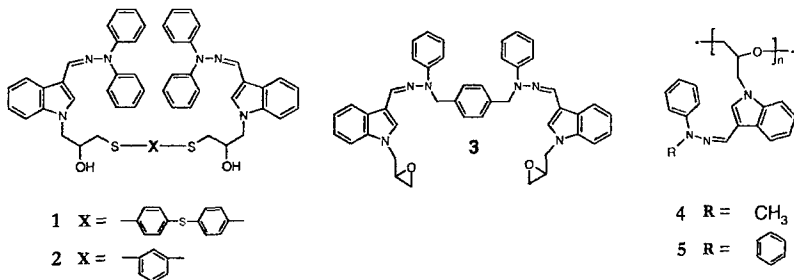
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Organic electroactive molecular glasses and oligomeric materials represent a rapidly expanding subject of research because of their present or potential application in various electronic and optoelectronic devices. In this work we have chosen indole as the main building block for the design and synthesis of hole-transporting low-molar-mass and oligomeric hydrazones. Indole as the moiety was mainly employed in photorefractive systems^[1,2] and only little investigations have been done on indolyl-containing hydrazones as charge-transporting materials. The aim of our work was synthesis and investigation of the properties of new glass-forming indole-based hydrazone compounds. 1-(2,3-Epoxypropyl)-indole-3-carbaldehyde N,N-diphenylhydrazone, 1-(2,3-epoxypropyl)-indole-3-carbaldehyde N-phenylhydrazone and the twin molecules obtained by the interaction of these epoxy derivatives with different linking agents are reported. The structures of the newly synthesized indole-based hydrazones are shown below. The values of ionisation potentials measured by electron photoemission technique are in the range from 5.41eV to 5.55eV. The charge mobilities were estimated by the xerographic time of flight technique. The reported hydrazones showed moderate charge transport properties. For example, hole drift mobilities in the 50 wt. % solid solution of **1** in bisphenol Z polycarbonate reached $1.0 \cdot 10^{-6} \text{ cm}^2/\text{Vs}$ at high electric fields.

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Ytterbium (III) trifluoromethanesulfonate was used as initiator for cationic polymerization of 1-(2,3-epoxypropyl)-indole. The followed polymer analogous reactions i.e. Vilsmeier formylation and condensation with different hydrazines enabled to synthesize oligomers **4** and **5**. The thermal, optical and photoelectrical properties of the oligomers have been studied.

MICROOPTICAL SURFACE MAKING BY UV-CURING OF MONOMERIC COMPOSITIONS IN NEAR FIELD OF COHERENT LIGHT SOURCE

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Recently the new raster optical elements based on polymeric microoptical surface like microlenses arrays, reflective optics arrays and Fresnel optic arrays are widely investigated. The mostly promising and interesting field of practical application of microoptic is development of method of optical microelements formation on the top of the fiber for its coupling with semiconductor laser and planar single mode waveguide. It is important a possibility of formation of optical element coaxial with it axis without positioning process.

We was developed a new method of microoptical surface formation based on dosed UV-curing of monomeric acrylic composition having specific interaction with substrate, for example with glass substrate. In this method surface of cured polymer grown from glass substrate to volume of liquid monomer mixture with exact border between cured and uncured material. Profile of created optical surface will be determine by distribution of UV light in the field of photomask, so any needed profile of microoptical surface can be prepared with suitable distribution of

UV light. Height of optical surface dependence from the optical transmission of photomask is shown in the Fig. 1.

Developed method allows making microlenses on the top of the fiber at curing of liquid monomer composition on its top by UV light come out from the fiber. As cone of UV light come out from the fiber is coaxial with its axis,

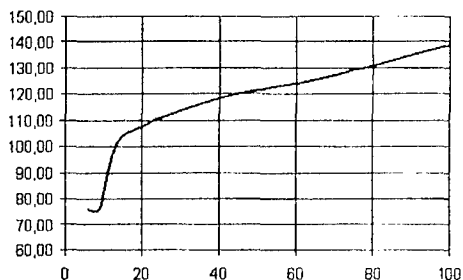


Fig. 1. Dependence of optical surface height (microns) from the optical transmission of photomask

microlens formed on its top is coaxial with its axis also. Profile of optical surface of microlens can be adjusted by aperture of light incoming to fiber and the time of exposure. In Fig 2 process of microlens grown in the top of the fiber is shown.



Fig. 2. Photo of microlens on the top of fiber depend upon the time of exposure (increase of time of exposure – from left to right)

The work was made under support of RFBR Project # **05-02-08048** “Investigation of electro-optic nanostructures with high hyperpolarizability based on nanocrystals density packing in polymer matrix for use in microwave optoelectronic elements” and Project of Russian Federal Agency of Education # **RNP.2.1.1.1403** “Investigation of optical surface formation in near field of coherent light source by photo curing of monomeric compositions”.

WELL DEFINED CARBAZOL-3,9-DIYL – BASED OLIGOMERS AS HOST MATERIALS FOR ORGANIC ELECTRO-PHOSPHORESCENT DEVICES

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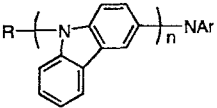
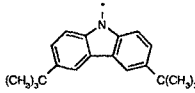
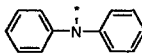
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Electrophosphorescent light-emitting diodes (LEDs) have been attracting much attention because of their high quantum efficiency, which can theoretically approach 100% [1]. Unlike electrofluorescence, electrophosphorescence can make full use of both singlet and triplet excitons owing to strong spin-orbital coupling of heavy-metal ions in phosphorescent complexes. In phosphorescent LEDs the triplet emitters are normally used as emitting guests in a host material. The triplet level of the host must be larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host. As such, effective host materials reported for the latter devices are limited within few structural features such as carbazole or phenylsilane based derivatives.

In this presentation, we report the new molecular design for large triplet energy gap materials. The structures of carbazol-3,6-diyl based oligomers (**M2-3**) shown in Table 1 were synthesized via modified Ullmann [2] coupling reactions as we have described earlier [3]. Carbazole dimer **M1** with peripheral butyl groups, which improve morphological stability of the amorphous material, was prepared by the Ullmann procedure from 3-iodo-9-ethylcarbazole and excess of 3,6-di(*t*-butyl)-9H-carbazole.

Table 1

Materials		n	R	NAr
 General structure	M1	1	C ₂ H ₅	
	M2	2	C ₂ H ₅	
	M3	2	C ₆ H ₄ - <i>p</i> -OCH ₃	
	M4	3	C ₂ H ₅	

All four compounds show high decomposition temperatures over 320 °C in thermogravimetric analysis and distinct glass transitions (with *T_g*'s of ~103-123 °C) in differential scanning calorimetry, indicating that they are truly stable amorphous materials as desired for LED applications. The carbazole dimer **M1** has relatively large triplet energy of 2.95 eV (i.e. the transition energy of T₁→S₀

estimated from the highest-energy phosphorescence peak). The oligomers **M2-3** with diphenylamino end-cap show a significant red shift in phosphorescence, leading to a substantially lower triplet energy of ~2.71 eV. We have used Ir(ppy)₃ doped in **M1** as the emitting layer for green phosphorescent LED. Rather high brightness of 25000 cd/m² and turn-on voltage of ~3.5 V indicate an effective carrier injection into emitting layer. The maximal EL quantum efficiency of the device is 16 cd/A and the power efficiency reaches 7 lm/W.

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POLYMERIC MATERIALS FOR RECORD OF THE BIREFRINGENCE PHASE IMAGES

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We consider what is the spectral dependence of the Mueller matrix of the circular Polaroid CP-HN in the visible region, and how allowing for it one can describe colors of the latent marks images that become apparent while observing through the Polaroid on birefringent stickers for identification of products of printing industry. We determine the matrix spectral dependence with taking account of the spectral properties of Polaroid films. Based on calculations performed with use of the obtained matrix, we note the images color features that can be observed through the CP-HN on a spectral-neutral identification sticker.

Object of research are the polymeric photosensitive materials for record birefringence of the phase images.

The aim of the present work is the updating of laboratory technology of receiving of a polymeric material used for record birefringence of the phase images, for increase of scales of synthesis, and also operating time of an experimental batch of a material.

The basic methods of research are: methods of organic chemistry, methods of chemistry of polymers.

As a result of the carried out work:

The laboratory technology of receiving of a polymeric material used for record birefringence of the phase images is modified at the increased scales of synthesis.

On the developed modified laboratory technology of synthesis of a polymeric material for record birefringence of the phase images the experimental batch of molecular weight 500 was received.

The results can be used at an operating time of experimental batches of a polymeric material used for record birefringence of the phase images, and also at scaling laboratory technologies.

The receiving monomer is the basic limiting factor at scaling synthesis is out, requiring proportional increase of volumes reactor at growing quantity of substances.

NOVEL ORGANIC AUTOCOMPLEXES AND METAL CHELATES ON THE THEIR BASE : SYNTHESIS AND CHIRAL OPTICAL PROPERTIES

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The organic compounds with intramolecular charge transfer, so-called autocomplexes, where the electron donating and accepting moieties are combined into one and the same molecule have attracted significant scientific and technological attention over the years. In this study the improved methods for the synthesis of a large number of the new autocomplexes, having nitroaromatic acceptor fragments (dinitroquinoline and picrylic type), various on nature and strength donor fragments and chiral label in bridged groupings have been developed. The conformational polymorphism phenomena in the series of these compounds has been investigated. The preparation of the differently coloured crystalline modifications - potential non-linear optical (NLO) material are carried out under carefully controlled conditions in different organic solvents and their mixtures. The analysis of the luminescence data shows, that anomalous Stokes shift (up to 5000 cm^{-1}) founded for one of these polymorphs to be due to the form derived via intramolecular proton transfer in the excited state.

The organic autocomplexes with chiral label in bridged groupings were obtained in the both enantiomeric forms on the base of optically active α -phenylethylamine and some it's derivatives. The chiral optical properties were investigated.

The series of autocomplexes with aromatic and heterocyclic donor fragments are chosen firstly as ligands for synthesis on the their base of the new type metal chelates Cu(II), Ni(II), Co(II), Zn(II) with N,N-coordination of chelate rings. The preparation of the metal chelates were carried out in accordance to the classical method in solution and by electrosynthesis using sacrificial anodes.

Using a number of physicochemical methods - X-ray diffraction method, UV-vis, NMR spectroscopy, FTIR experiments, fluorescence spectra and electrochemical measurements a specific information on details of the electronic and spatial structure of the autocomplexes as ligands on one hand and metal-chelate on the other has been obtained. According to these results the linear correlation between values of the intramolecular charge transfer energy and the ionization potential of donor fragment has been established. The unknown ionization potentials of the number of donor compounds have been experimentally determined. A regulation in the intramolecular charge transfer as well as its nature have been investigated.

Finally, the results presented here clearly demonstrate, that the molecules of these compounds as ligands-autocomplexes, so and metal chelates on the their base have a conformation in which two type of charge transfer transition have been revealed: through the conjugated bond system and by contact way through a space ("contact charge transfer").

WELL DEFINED CHARGE TRANSPORTING AMORPHOUS MOLECULAR MATERIALS FROM 1,3-INDANDIONE

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E. Montrimas²

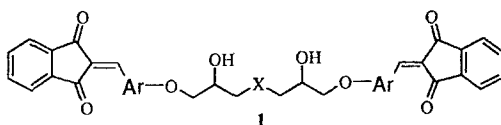
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Organic charge-transporting materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices and other optoelectronic devices [1]. Along with the photoconductive properties, the morphological stability is also important in determining their potential applications in optoelectronic devices. Thin films based on crystalline compounds or materials having large crystalline domains tend to degrade these devices. For that matter polymeric materials are better: good quality polymer films can be generated from solution deposition techniques, they are usually glassy and have good mechanical

properties. The main drawback encountered with polymers in optoelectronic devices is their chemical purity. The impurity trap charge carriers lead to a decrease in the device efficiency, stability and its lifetime. Another problem in preparation of the thin films is poor solubility of polymeric materials in the common organic solvents. Recently a lot of attention is paid to organic low molar mass compounds which are stable amorphous materials above room temperature. Such compounds are called molecular glasses [2]. They are pure materials with well-defined molecular structures and definite molecular weights without any distribution.

In contrast with hole transporting molecular glasses, there are only a few studies on electron transporting molecular glasses. In this work we report on the synthesis of novel molecular glasses containing indan-1,3-dione moieties that allow to exhibit electron transport and excellent film-forming properties.



The general synthesis of newly designed molecular glasses containing 1,3-indandione moieties involves the reaction of aromatic aldehyde comprising hydroxyl group with epichlorohydrin followed by typical condensation with indan-1,3-dione. Finally, the difunctional nucleophilic agents (H-X-H) were used for linking two previously obtained oxiranes to form the final products, represented by general formula 1.

The goal materials are soluble in the common organic solvents. This is mainly due to the flexible linking fragments between chromophores. Clear, homogenous films of 1 were obtained by the casting technique. The photoelectric properties of the 1 were preliminary studied using such films. The charge mobilities measured in these amorphous films reach $10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at strong electric field.

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POLYMER FIELD EFFECT TRANSISTORS WITH POLYSILANE CHANNEL

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Polymer electronics is one of the major challenges in the present research into advanced electronic materials. Devices based on conducting and photoconducting polymers are supposed to be cheaper than conventional silicon-based electronics, at the same time having some special properties like easier processability, flexibility and possibility of manufacturing large area devices [1]. Among them, of a particular interest are those whose properties can be controlled by light.

One of the ways of fabrication of light-sensitive electronic elements is addition of photoactive molecules to an electroactive material. In the case of photochromic spiropyrans, absorption of light induces reversible structural changes of spiropyran molecules, followed by a large increase in their dipole moments. Placing spiropirane in the vicinity of the polymer chain may induce charge carrier traps, decreasing the carrier mobility [2, 3].

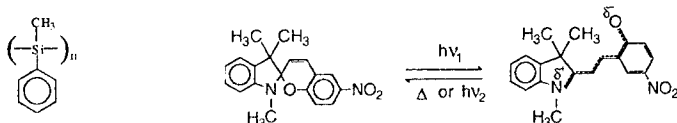


Fig.1. Structures of photoconducting poly(methyl-phenylsilane) and photochromic spiropyran

This contribution presents preliminary results of measurements on Field Effect Transistors (FET) whose conducting channel was made of poly(methyl-phenylsilane) (pMPSi) photoconducting polymer, both pure and doped with spiropyran. Current-voltage characteristics were measured in the dark and under illumination with several wavelengths.

The work was supported by the Polish State Committee for Scientific Research (Grant No 3 T08E 084 30). The author also thanks Professor Stanislav Nešpůrek (Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague) for the gift of pMPSi, and the British Council (Young Scientists Programme 2005) and Professor Martin Taylor for enabling him to visit the University of Wales Bangor and to fabricate the substrates used in this study.

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NEW ORGANIC ELECTROLUMINESCENT MATERIALS BASED ON CHELATE METAL COMPLEXES

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The study of organic electroluminescent materials is now a rapidly developing field of science due to promising practical applications in organic light-emitting diodes (OLED). In spite of impressing achievements of the last decade, the problem of searching of the new materials an structures for organic electroluminescent devices is still actual. In the present work, we report the synthesis of some new materials and the study of their electroluminescent properties.

Active electroluminescent materials should possess an efficient luminescence and good electron transport properties. Among these materials, chelate metal complexes play an important role. Chelate complexes used in OLED devices usually contain heterocycles with nitrogen and oxygen atoms. An example is a well-known aluminum 8-hydroxyquinolate (Alq) and other compounds based on 8-hydroxyquinoline. It is of interest to prepare compounds containing other heteroatoms instead of oxygen atoms in chelate cycles for OLED applications.

We have synthesized some new metal complexes based on 8-mercaptoquinoline and 8-aminoquinoline derivatives with different metals (Zn, Cd ,Ga) and studied their spectral and electroluminescent properties. Some new complexes based on oxygen containing cycles were also prepared. The new compounds are characterized by blue and green luminescence. OLEDs prepared on the base of the new materials exhibit bright light emission with the effectiveness about 10 cd/A.

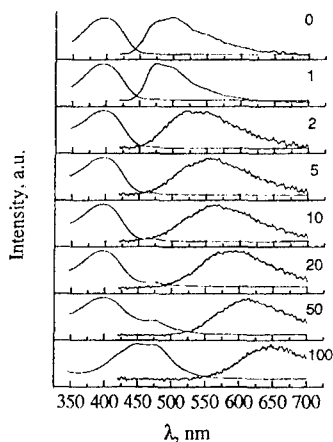
This work was supported by PPR "Fundamental Problems of Physics and Chemistry of Nanometric-Scale Systems and Materials".

COLOR TUNING IN OLED DEVICES BASED ON NEW PERYLENE DERIVATIVES

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Perylene dyes are of interest because of their high photostabilities and fluorescence quantum yields. Recently, applications of such materials for organic light-emitting diodes were reported [1,2].

We have synthesized some new perylene derivatives – perylene 3,4,9,10-tetracarboxylic acid esters [3], studied their spectral properties and used them in light-emitting device. The light-emitting properties were studied for mixtures with the zinc chelate complex $\text{Zn}(\text{OBBA})_2$ which obtain good electron-conducting properties and is a good host matrix for organic dyes [4].



Mixing of perylene derivatives with $\text{Zn}(\text{OBBA})_2$ gives a possibility to obtain different colors of light emission. As an example, the absorption and photoluminescence ($\lambda_{\text{exc}}=370$ nm) spectra of the films made of the mixtures of $\text{Zn}(\text{OBBA})_2$ with perylene 3,4,9,10-tetracarboxylic acid tetraethyl ester are shown in the figure (digits near the curves are the percentage of the ester). Maximum of emission continuously shifts to long wavelength with rising of the ester contents.

We have also prepared the electroluminescent devices based on mixtures of perylene derivatives with $\text{Zn}(\text{OBBA})_2$ and obtained the emission with efficiency about 0.25 cd/A.

This work was supported by PPR "Fundamental Problems of Physics and Chemistry of Nanometric-Scale Systems and Materials".

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FLUORENYL-CONTAINING CHARGE TRANSPORT MATERIALS FOR OPTOELECTRONIC APPLICATIONS

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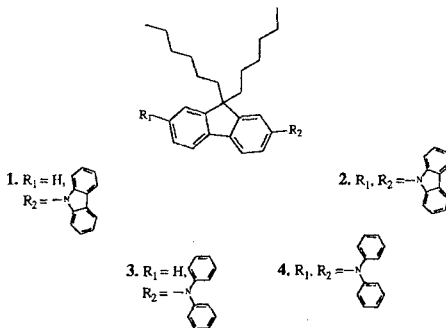
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Polyfluorenes and fluorenyl-containing aromatic amines have attracted much scientific and technological interest during the past five years because of their potential applications in optoelectronic devices [1,2]. In this presentation we report on the synthesis and studies of aromatic amines with fluorenyl group.

Fluorenyl-containing aromatic amines **1-4** were prepared by two-step reaction involving alkylation of mono- or dibromofluorene followed by Ullmann coupling reaction of carbazole or diphenylamine with mono- or dibromodihexylfluorene.



The chemical structures of the synthesized compounds was confirmed by ¹H-NMR, ¹³C-NMR and IR spectroscopy. Some of these compounds form glasses. Their ionisation potentials range from 5.86 eV to 6.1 eV. Hole drift mobilities of 50 % solid solutions of some synthesized aromatic amines in bisphenol Z polycarbonate established by the xerographic time-of-flight technique at high electric fields (10⁶ V/cm) exceed 10⁻⁴ cm²/Vs.

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INVESTIGATION OF ADSORPTION PROPERTIES OF THIN FILM GAS SENSORS BY COMPUTER HOLOGRAPHIC INTERFEROMETRY

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The work is devoted to investigation of adsorption properties of interferometric gas sensors based on the thin calixarene sensitive films under influence of some organic analytes by computer holographic interferometry. It's direct method of film's optical path length measurement and it don't need to use any initial model knowledge about film.

The method is based on the receipt of phase portrait of the film by Fourier transformation and filtration of intensity distributing in the interference picture. Analysis of picture by using of bearings bands method include comparison of analysed sample interferogram in the initial stage with sample interferogram after analyte exposure. For the construction of phase portrait of the film the sample was made of two parts: one half was covered by film, a pure substrate served as other one. Film's exposition by analyte vapors was carried out in a close cell during 10-30 min. at a temperature about 20 °C. To increase the measurements accuracy the resulting phase change was determined as a difference of phase changes in the analysed film and on the area of the sample free of film.

The optical parameters of thin calix[4,6]arene films were investigated through measuring of optical path length in films during their saturation by ethyl and butyl alcohol vapors. The qualitatively different behavior of the calixarene-alcohol complex for both analytes is shown resulting in increasing of effective optical path for ethanol and decreasing one's for butanol (Fig.1). Influence of calixarene film thickness on the interferometry response value was studied. Features of molecular complexes of calixarenes with ethanol and butanol are shown by a molecular computer simulation, which are correlated with the experimentally obtained responses.

A qualitative model is suggested, that explain the experimental facts by a change a molecular refraction and volume of host-guest complex. It can be accompanied by considerable mechanical tension of film in the presence of alcohols with different molecule volume that is affecting subsequent analyte adsorption.

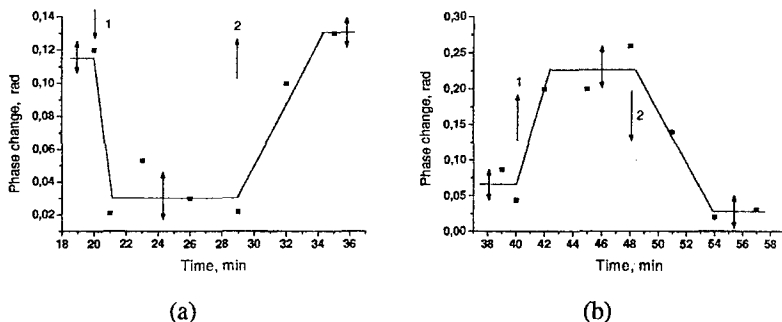


Fig.1. Phase change for calix[6]arene film upon exposure to saturated butanol (a) and ethanol (b) vapors: 1 – injection of analyte, 2 – recovery in air; film thickness is 150 nm.

CONDENSED AROMATIC AMINES AS ELECTROACTIVE MATERIALS FOR OPTOELECTRONIC APPLICATIONS

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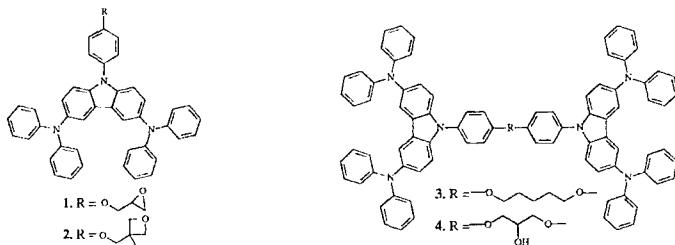
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Among hole-transporting materials used in optoelectronic devices aromatic amines have attracted most attention of researchers. Hole transport materials which do not readily crystallize are preferable for these application. The stability of amorphous state of such materials can be enhanced either by increase of molecular size of molecular glasses or by polymerization of electroactive monomers. In this presentation we report on the synthesis and studies of condensed aromatic amines with reactive functional groups. We also show a possibility of the preparation of hole-transporting amorphous molecular materials by twinning these compounds.

Condensed aromatic amines **1-4** were prepared by multistep synthetic route involving the iodination of 9-(4-methoxyphenyl)carbazole using KI and KIO₃, Ullmann coupling of diiodo derivative with diphenylamine, demethylation, alkylation (for **1**, **2** and **3**) and the reaction of epoxy compound **1** with compound containing hydroxyl group (for **4**).



The chemical structure of all the compounds reported was confirmed by 1H -NMR, ^{13}C -NMR and IR spectroscopy. All these compounds form glasses. Their thermal, optical, photophysical and photoelectrical properties have been studied. The ionisation potentials range from 5.3 eV to 5.4 eV. Hole drift mobilities of 50 % solid solutions of some reported in this presentation aromatic amines in bisphenol Z polycarbonate established by the xerographic time-of-flight technique exceed $10^{-5} \text{ cm}^2/\text{Vs}$ at high electric fields (10^6 V/cm).

NEW THIOPHENE-BASED GLASS-FORMING COMPOUNDS FOR OPTOELECTRONIC APPLICATIONS

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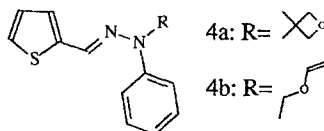
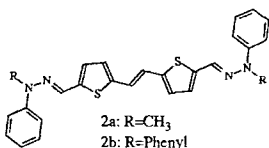
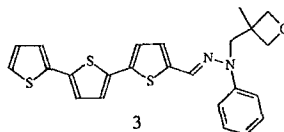
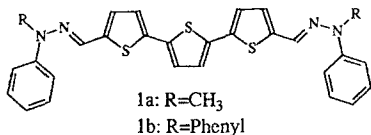
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Organic charge-transporting materials are used in optoelectronic and electronic devices like organic light-emitting diodes, photovoltaic cells, field effect transistors and other devices [1]. It is known, that the presence of sulphur or oxygen atoms in the molecules of organic semiconductors improve their physical-mechanical properties. [2]. Thiophene-based glass-forming hydrazones represent a relatively class of organic hole-transporting materials and can be used for optoelectronic applications, e.g., in electrophotographic photoreceptors [3,4].

In this presentation we report on the synthesis and characterization of new hole-transporting molecular glasses, having thiophene moieties.

New hydrazones, the structures of which are shown below, were synthesized through Mc Murry coupling (**2a**, **2b**), Vilsmeier formylation, condensation of the formyl derivatives with hydrazines having different substituents and alkylation with 3-bromomethyl-3-methyloxetane (for **3**, **4a**) or with 2-chlorethylether (for **4b**).



The chemical structures of synthesized compounds were confirmed by ¹H NMR and IR spectroscopy. The optical, thermal and photoelectrical properties of the obtained materials are reported. The ionization potentials of thin films of the synthesized hydrazones established by the electron photoemission in air technique are in the range of 5.43-5.76 eV. Time-of-flight hole drift mobilities in molecularly doped polymers containing 50 wt. % of some synthesized hydrazones exceed 10⁻⁵ cm²/Vs at high electric fields.

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NEW GLASS-FORMING ELECTROACTIVE ENAMINES

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Electroactive molecular glasses are being widely explored as well as used in copiers, laser printers, organic light-emitting diodes, photovoltaic devices, and in photorefractive compositions. Among p-type organic semiconductors, enamines, although not yet widely studied, are significant as compounds having

extraordinarily good charge-transporting qualities. Enamines represent a class of donor molecules that contain $N-C=C$ functionalities. It was of particular interest to synthesize new potentially charge-transporting enamines. In this presentation we report on the synthesis and properties of seven new enamine molecules.

The reported enamines were synthesized by the reaction of the corresponding diamines with diphenylacetaldehyde or methylphenylacetaldehyde in the presence of a catalytic amount of \pm -10-camphorsulphonic acid.

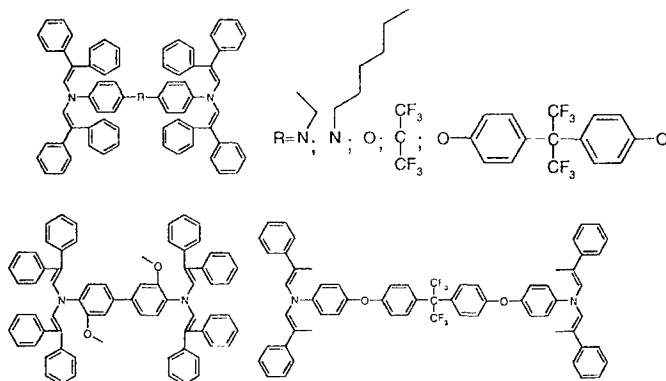


Figure 1

The chemical structures of the synthesized compounds were confirmed by 1H -NMR, IR and mass spectrometry.

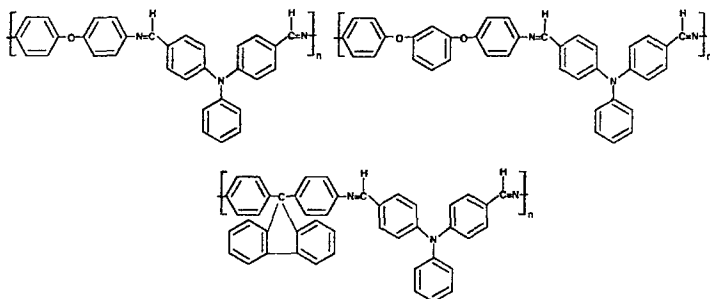
Most of the synthesized compounds form glasses as established by the differential scanning calorimetry. Amorphous films of the molecular glasses can be prepared by the simple casting technique. The newly synthesized compounds generally exhibit very high thermal stability as well as high glass-transition temperatures. Their ionisation potentials are in the range from 5.1 eV to 5.7 eV. Charge transport properties of the selected enamines were studied by the xerographic time of flight technique. Hole drift mobilities in the solid solutions of the new compounds in bisphenol Z polycarbonate exceed $10^{-6} \text{ cm}^2/\text{Vs}$ at high electric fields.

SUPRAMOLECULAR MODIFICATION OF OPTICAL PROPERTIES OF SOME NEW POLYAZOMETHINES

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Significant progress in synthesis of light emitting polymers has been observed since 1990 when light emitting diodes (OLED) were discovered. However, despite of this searching for new polymers is still a challenge. In particular blue light emitting polymers are deemed desirable because it is generally more difficult to prepare LED from inorganic materials. On the other hand full color exhibition and white light devices need blue light [1]. Among the blue light emitting polymers triarylene-based conjugated ones are very interesting [2, 3].

In our work a series of new polyazomethines bearing triphenylamine moieties was synthesized and influence of the polymers chains structures along with their supramolecular modifications on optical properties, mainly photoluminescence was investigated. The structures of the polyazomethines being polycondensation products of 4,4'-diformyltriphenylamine with diamines are presented below:



The polyazomethines are soluble in many solvents (DMA, chloroform) and form transparent, flexible foils.

Supramolecular modifications of the polyazomethines were done by doping with phenolic type compounds: p-chlorophenol and m-cresol, being able to form H-bond with lone electron pairs of nitrogen atoms in polymer chain. The polyazomethines emitted light with wavelength in the range of 460-470 nm. After doping a little shift of wavelength was observed. However intensity of the photoluminescence increased significantly.

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INVESTIGATIONS OF POLYMERS BEARING NLO CHROMOPHORE UNITS AS HOLOGRAPHIC MATERIALS

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In the last years a considerable amount of research has been directed toward the development of the functionalized polymers, which contain optically active units – chromophores. It is intension to use this kind of polymers as optical information storage, optical information processing, aligning layers for liquid crystals, optical switching devices and diffractive optical elements among others [1]. Special attention has been paid to the photochemistry of azobenzene-containing polymers. Many of optical applications are possible due to efficient photoisomerization and photoinduced anisotropy of the azobenzene groups. Since the observation of the holographic formation of amplitude and phase gratings in those materials including surface relief gratings (SRG), the functionalized azopolymers were found as a new class of holographic materials. It is expected that holography is the most promising technique for establishing photonics as a future technology [2].

The optical response of the polymer is strongly influenced by its chain structure and structure of the chromophores. In connection with this it is necessary to develop the new types of functionalised polymers in order to find compromises in the polymer compositions with respect to the requirements of the different applications. The various strategies in the design and synthesis of polymers bearing azobenzene groups have been applied [3-5].

In this work a series of new thermally stable polymers bearing azochromophore group as a side chain bonded to main chain via amide or ester linkage were prepared and their properties mainly ability of holographic grating recording were investigated. It was found that kinetics of grating recording depends strongly on the group bonding the chromophore in the main chain: much faster were recorded gratings when chromophore was bonded via amide linkages than via ester one.

The polymers were characterised by FTIR, NMR, DSC, UV-VIS, and elemental analyses. The polymers exhibit good thermal stability, solubility in common solvents and film forming properties.

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$T_g = 103\text{ }^{\circ}\text{C}$ for 2). These compounds exhibit high charge carrier mobility ($\sim 10^{-5}\text{ cm}^2/\text{Vs}$ at $E = 10^6\text{ V/cm}$), good film-forming properties and could be used in the organic photoreceptors without binder materials.

**FEATURES OF ELECTROLUMINESCENCE OF NEW BLUE
POLY (9,9-DIOCTYLFLUORENYL-2,7-DIYL) - END CAPPED WITH
POLYHEDRAL OLYGOMERIC SILSESQUIOXANES**

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The emission of new blue polymer poly (9,9-dioctylfluorenyl-2,7-diyl) end capped with polyhedral oligomeric silsesquioxanes, (PFO-POSS) has been investigated. Thin films of PFO-POSS showed pure blue photoluminescence (PL) with structured spectrum and maximum at $\lambda_{\text{PL}} = 423\text{ nm}$. However, the OLED structures formed on the PFO-POSS base emitted green light with broadened spectrum and maximum at $\lambda_{\text{EL}} = 510 \sim 529\text{ nm}$. The origin of the green EL emission was identified as an emission from defects caused by oxidation degradation and cross-linking of the polymer chains. It suggests that the energy traps on the cross-linked chains play an important role in PFO-POSS emission, and their formation could not be completely suppressed by end capping of PFO backbone with POSS bulky groups.

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NEW METHACRYLIC OXAZOLONE CONTAINING MONOMERS

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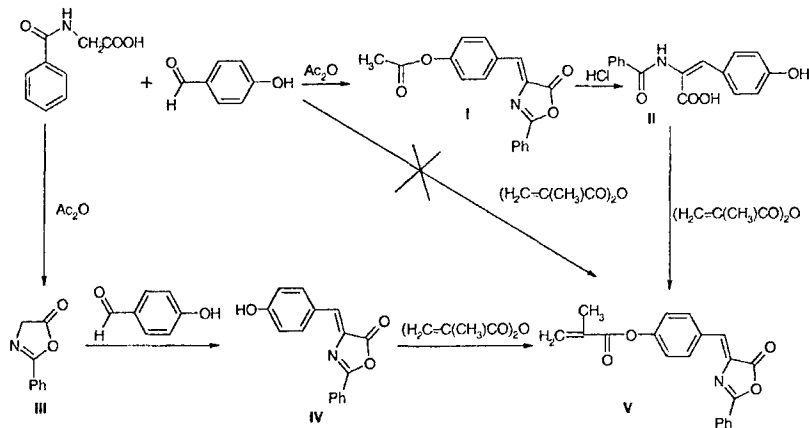
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Nowadays an increasing practical interest is represented by polymers which fluorescent characteristics can be saved in time during their exploitation. Such properties can have polymers which contain 4-benzylidene-2-phenyloxazolone fragment, because compounds that contain it have yellow-orange luminescence in the solid state.

Under action of light for phenyl methacrylates and their polymers rearrangement of their molecules with formation of α -ketonic structures is observed. For clarifying of photochemical properties the synthesized acylated products of condensation of p-hydroxybenzaldehyde and hyppuric acid were found:



It was shown that on condensation of last ones after standard methods in acetic anhydride acylated product appears. And, but at their interaction in methacrylic anhydride the final product V does not appear. Except of removal of acetic group (product I) in soft conditions oxazolone cycle opens up with formation of colorless product II. His heating in a methacrylic anhydride gives a final monomer V.

The second way of obtaining of methacrylate V consists of the cyclization of hyppuric acid in acetic anhydride, condensations of 2-phenyloxazolone III that appeared with p-hydroxybenzaldehyde and acylation at heating.

The structure of all obtained compounds was proved by HNMR spectroscopy. Metha-derivative of V was obtained for which kinetics of copolymerization with butyl methacrylate was studied.

NOVEL CHARGE TRANSPORTING MATERIALS CONTAINING PHENYL-1,2,3,4-TETRAHYDROQUINOLINE MOIETIES

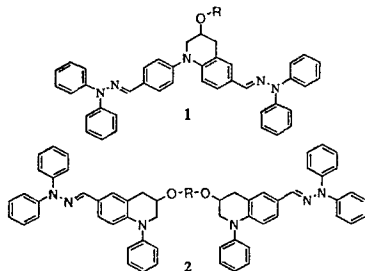
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Recently, because of their rapid charge transporting ability, more attention has been paid to organic photoreceptors with hydrazones possessing 1-phenyl-1,2,3,4-tetrahydroquinoline moieties as hole transporting materials (TM) [1]. Unfortunately, the multi-step synthesis of the starting 1-phenyl-1,2,3,4-tetrahydroquinoline limits the development of organic photoreceptors with this promising moiety.

A simple, one-pot reaction synthesis procedure of 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline was performed at Organic Chemistry Department of Kaunas University of Technology. The hydroxyl group at the 3-position of this starting material allows to develop and evaluate a novel families of hole transporting materials for electrophotography having the following structures.



Formation of the glassy state of 1 and 2 was confirmed by DSC analysis. These investigations revealed that 1 can exist both in crystalline and amorphous state while compounds represented by structure 2 were found only in amorphous phase in our experiments. The molecular glasses 1 and 2 are soluble in common organic solvents such as chloroform, THF, dioxane and etc. This really good solubility is mainly due to the flexible tetrahydroquinoline core and linking fragments between chromophores. The samples for the charge carrier mobility measurements were prepared by casting the solutions of 1, 2 or solutions of the mixtures of these compounds with binder material polycarbonate or polyvinylbutyral at a mass proportion of 1:1 in THF. The highest hole-drift mobility in the newly synthesized TM exceeds $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of 106 V cm^{-1} was observed in the molecular glasses with structure 1.

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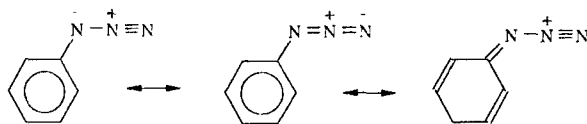
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SENSITIVITY OF ORGANIC AZIDES TO DIFFERENT BANDS OF SOLAR SPECTRUM

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Solar radiation is one of the most important ecological factors affecting on human health, biological processes and materials ageing [1]. UV band of its spectrum can be divided (by CIE, 1970) on the following ranges: UVA from 315 to 400 nm, UVB from 280 to 315 nm and UVC from 100 to 280 nm. UVC range completely and UVB partially are absorbed by stratospheric ozone layer. UVA can't do it and therefore it's more dangerous. So that the importance of their distinguishing is obvious.

Organic azides are very suitable as actinometric compounds for UV radiation. In the ground state azidogroup has quasi-linear geometry and significant positive charge on the two terminal nitrogen atoms [2]. These are main structures in equilibrium:



In the excited state the first unoccupied orbital can be populated, but it depends on the size and charge of the aromatic system. For the initial members of azides series this orbital is always populated and these azides are photoactive, they decompose under UV irradiation. With an increase in the size of the aromatic system azides can become photo-inactive [3].

Some series of organic azides were synthesized and investigated in our university which have high photosensitivity in the various ranges of the UV spectrum [4]. Azides of phthalimide [5] or fluorane series have several absorption maxima and are sensitive to full UV band (all ranges). Such azides as 2-azidoxanthone (as well as studied by us pentazadienes) with a single maximum are sensitive to UVA range (315 - 400 nm). Another ones as derivatives of biphenyl or nitrobenzthiazole with conjugated aromatic cores have sensitivity to UVB range (280 - 315 nm). Some heterocyclic sulfonylazides are sensitive to UVC range (100 - 280 nm). Among them series of sulfonyl azides with two or three non-conjugated aromatic rings were studied and phenomenon of intramolecular energy transfer influence on azides sensitivity was discovered. Due to this phenomenon good possibilities to direct sensibilities of organic azides have been found.

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INTERFERENCE GAS SENSOR BASED ON SENSITIVE CALIXARENE FILMS

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Recently we can observe intensive search of new methods of the analysis of gas mixtures, in particular, using of thin film color interferometry [1]. The idea of this method is based on the comparative analysis of the color characteristics of signals, obtained as the result of an interference of white light in a thin layer of the colored sensitive material both at the absence of the analyzed substance and after interaction with this one.

The purpose of this work is the research of the opportunity of definition of optical parameters of the thin sensitive films of calixarenes (thickness and the refraction coefficient) by means of color R, G, B interferometry, the studying of interaction of analyte-calixarene type and also in the optimization of metrological characteristics of the developed colorimetric sensors, mainly, stability and reproducibility of the responses. The task of this work is also to develop new modified methods of image processing of the multielement sensors for realization of systems of automatic recognition of chemical images based on the generated images database.

Films of tertbutyl calixarene of 4, 6, 8 types with thickness of 50-300 nanometers are obtained by thermal evaporation in vacuum with the subsequent

deposition on the silicon polished substrates. As the result of this work the sensor abilities of the array on the basis of above three types of calixarene films to a number of organic analytes (alcohols, ketons, aromatics) are demonstrated.

The modeling of quantitative values R , G , B factors of reflected light depending on changes of optical parameters of a sensitive film was carried out. We assumed that molecule adsorption changes either thickness or refraction coefficient of the film. The calculations have shown that interaction with alcohol molecules results in increase of calixarene film thickness up to 10 nanometers, and to decrease of the refraction coefficient approximately by 0.03. The obtained results allow to make a decision about interaction of calixarene film with molecules of alcohols as reversible complexation of type the guest-host without considerable change of a microstructure of the calixarene film.

It is shown that preprocessing of calixarene films in acetone vapor causes reversible changes of thickness and refraction coefficient of the films and is not accompanied by reconstruction of their microstructure. As the result it leads to essential increase of sensor sensitivity to alcohols.

As the result of this work an approach to creation of the portable interference gas sensor based on the CCD camera and thin sensitive calixarene films was developed. For the improvement of the received information accuracy the normalizing phase method of CCD camera image processing have been developed, which take into account the time instability of the source of illumination and presence of the noise in data communications tracts. The developed procedure of image processing gives the possibility of recording, processing and viewing of received images in dynamics during measuring time.

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TRIAZINE-BASED AROMATIC AMINES AS NEW GLASS-FORMING CHARGE-TRANSPORT MATERIALS

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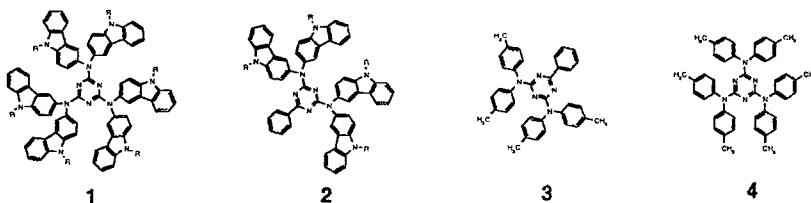
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1,3,5-triazine-based compounds are known as relatively effective electron-transporting materials^{1,2}. In this presentation the synthesis and characterization of new star-shaped 1,3,5-triazine compounds, containing aromatic amino groups are reported.

The 1,3,5-triazine-based compounds **1-4** were prepared via modified Ullmann coupling reaction of 2,4,6-triamino-1,3,5-triazine or 2,4-diamino-6-phenyl-1,3,5-triazine with an excess of 3-iodo-9-alkylcarbazole (for the synthesis of **1** and **2**) or 4-iodotoluene (for the synthesis of **3** and **4**).



Compound **1**: R=C₄H₉; **2**: R=CH₂CH(C₂H₅)C₄H₉.

The optical, thermal and photophysical properties of the synthesized compounds as well as photoelectrical properties of the charge transport layers prepared from the new materials are reported.

¹ T. Yamamoto, S. Watanabe, H. Fukumoto, M. Sato, T. Tanaka, *Macromol. Rapid. Commun.* 27 (2006) 317.

² Abhishek P. Kulkarni, Christopher J. Tonzola, Amit Babel, and Samson A. Jenekhe, *Chem. Mater.* 16(2004) 4556.

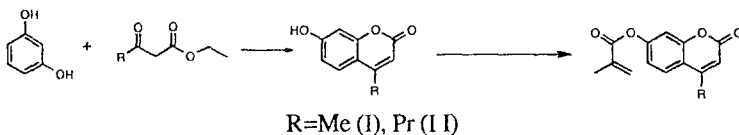
SYNTHESIS AND RESEARCHES OF POLYMERIC ACTIVITY OF MONOMERS ON THE BASIS OF 7-HYDROXY-2H-CHROMENONE DERIVATIVES

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Constant expansion of areas of polymeric materials applications, an increase of requirements to their operational characteristics, profitability and ecological purity put a problem of synthesis of polymers with special properties.

New methylacrylate monomers have been synthesized on the base of 7-hydroxy-4-methyl-2H-2-chromenone (1) and 7-hydroxy-4-propyl-2H-2-chromenone (2), and their ability to radical polymerization in a solution have been researched. Synthesis of these compounds was carried out using standard techniques, the structure was proved by spectral methods.



Kinetics of radical thermoinitiated homopolymerization of synthesized methylacrylates is investigated by the dilatometry at 80°C with 10 % AIBN in DMF in an atmosphere of argon.

The received data testify that our monomers can be actively polymerized having $K_Z = 2,8 \cdot 10^{-3}$ (I), $K_Z = 3,3 \cdot 10^{-3}$ (I I), that is approximately three times faster, than similar ones with a structure of unsubstituted phenyl methacrylate ($K_Z = 1,1 \cdot 10^{-3}$), and the yields of polymerization for one and a half hour were reached 53.6 % (I) and 47.3 % (I I).

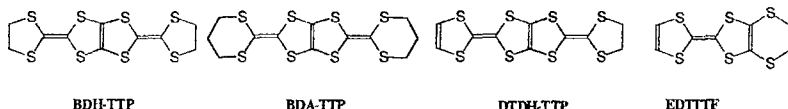
NEW ORGANIC CONDUCTORS BASED ON TETRATHIAFULVALENES AND TETRATHIAPENTALENES

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New electroconducting radical cation salts based on tetrathiafulvalene and tetrathiapentalene derivatives, namely, EDTTTF, BDH-TTP, BDA-TTP and DTDH-TTP, with halomercurate anions were synthesized and investigated. All of them are layered materials built of conducting layers of radical cations, which alternate with insulating layers of halomercurate anions. The resulting compounds exhibit a wide variety of electroconducting properties ranging from semiconductors, two-dimensional metals, a metal with a sharp transition to insulator, and a superconductor.



The BDH-TTP and DTDH-TTP halomercurates have $(\text{BDH-TTP})_4\text{Hg}_3\text{X}_8$, $\text{X}=\text{Cl}, \text{Br}$, $(\text{DTDH-TTP})_4\text{Hg}_3\text{Br}_8$ and $(\text{DTDH-TTP})_6\text{Hg}_3\text{Br}_9$ composition and show a metallic behavior of the temperature dependency of resistivity down to liquid helium temperatures. The BDA-TTP halomercurates of the $(\text{BDA-TTP})_4\text{Hg}_2\text{Br}_6$ and $(\text{BDA-TTP})_6\text{Hg}_4\text{I}_{10.34}$ composition are semiconductors with high enough values of room-temperature conductivities and activation energies being of 0.3 eV and 0.05 eV, respectively.

Recently [1,2] among EDTTTF iodomercurates we have found the crystals undergoing a superconducting transition near 8.1 K together with the crystals undergoing a sharp transition to insulator at 35 K. X-ray analyses at 90 K revealed the difference in the crystal structures and allowed us to ascribe the nonstoichiometric composition

$(\text{EDTTTF})_4[\text{Hg}_3\text{I}_8]_{1-x}$, $x = 0.02 \div 0.03$ to the superconductor and the stoichiometric one, $(\text{EDTTTF})_4\text{Hg}_3\text{I}_8$, to the metal with a transition to insulator.

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ELECTRICAL AND MAGNETIC PROPERTIES OF ARS TCNQ WITH PYRAZINIUM-BASED CATIONS

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Anion-radical salts (ARS) of TCNQ have been recently in attention focus due to their wide range of possible applications, and due to the discovery of ARS being capable of forming magneto-ordered structures[1, 2]. In spite of a long history of TCNQ chemistry, ARS with pyrazine derivative as a cation are not practically known. Pyrazine is the simplest analogue of phenazine (NMP), a constituent of the first organic metal – NMP-TCNQ.

ARS TCNQ with N-alkylpyrazinium cations represent a particular interest due to possessing such a nonalkylated nitrogen atom, a cation which may interact quite specifically with TCNQ⁻ anion-radicals or with donor-acceptor interaction of metal cations, that may result in the formation of supramolecular structures. Recently we have reported[3] the first ARS of TCNQ of a *quasi-two-dimensional* structure (all the previously known ARS of TCNQ are one-dimensional) – (N-Et-Pz)(TCNQ)₃. Quasi-two-dimensional character of this ARS follows from its structure and the analysis of its electro-physical and optical properties.

Some of the new ARS TCNQ (N-Me-2,5-di-Me-Pz)(TCNQ)₂, (N-Et-2,5-di-Me-Pz)(TCNQ)₂[4], (N-Me-2-NH₂-Pz)(TCNQ)₂, (N-Me-Tetra-Me-Pz)(TCNQ)₂, (N-Me-2,6-di-Me-Pz)(TCNQ)₂ and (N-Me-Tetra-Py-Pz)TCNQ₂ have been synthesized.

Crystal structure were determined for all of this compounds. Synthesized compounds were investigated by two experimental techniques: measurement of their absorption in the infrared (IR) spectral range and studies of the electric conductivity of the obtained samples.

For (N-Et-Pz)(TCNQ)₃ and (N-Et-2,5-di-Me-Pz)(TCNQ)₂ magnetic properties also were investigated and described.

Most of the synthesized compounds are quasi-two-dimensional semiconductors also. Some of this ARS possess a number of useful properties, such as relatively high electrical conductivity and low melting point. This properties allows to use the ARS in highly efficient electrolytic capacitors and other modern electronic devices.

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ELECTRONIC PROPERTIES OF NATURAL NANOPROTEIN STRUCTURES

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One of perspective directions of the development of organic materials electronics is the study of functional properties of natural pertinacious structures. Such examinations commute interest also for modern medicine, pharmacy, ecologies, as allow to reconsider sights on a role of protein in operation of the basic structures, including natural.

Proteomics is the new science studied the role of proteins in function of cells in natural structures.

The results of studies of optical, structural properties of natural protein - serum albumin are presented. The action on it of such physical factors as a laser radiation and electronic field (appearance of an electrophoresis) was also investigated. It is shown, that the water solutions of albumin are strongly ordered systems, which are very sensitive to an external influence. They easily change the structure, electronic properties under influence of physical fields. The influence of a solvent (water) on the structure of albumin and electronic properties of these structures has been investigated.

Is shown, that the optical examinations of crystal-optical properties of whey of albumin, other natural proteins allow really on molecular and electronic level to vary functional features of protein in natural cell-like structures.

The opportunities of practical application of electronic properties of different nanoprotein structures, which represent practical interest, in particular, for clinical proteomics have been proposed.

NANOCLUSTERS WITH BIOLOGICAL ACTIVITIES ON POLYMER SURFACES

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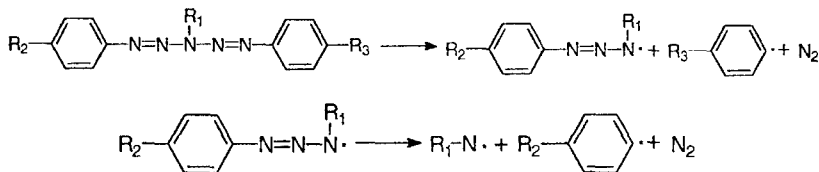
Coatings or films based on bioactive polymers can be applied in different fields, such as medicines, bioprotected constructive materials etc. The perspective way of their development is the polymer surface modification with clusters formation.

Organic azides and pentazadienes are known can generate free radicals under UV-irradiation which can initiate photopolymerization or grafting of their fragments on polymeric surfaces [1]. Series of new azides had been synthesized from commercially available sulfamide medicines, aminobenzoic and aminosalicyclic acids. They were characterized by spectral methods and their photolysis had been studied. In photolysis of organic azides nitrenes are obtained as primary products and molecule of nitrogen is evolved according to the scheme:



Accordingly to their structures azides can form singlet or triplet nitrenes but only the last ones can initiate the radical polymerization or grafting [2]. Such azides have usually carbonyl or sulfonyl groups connected with the benzene ring and we have synthesized and characterized some groups of these azides. Processes of the intramolecular energy transfer in their molecules were also studied and their influence on photochemical activity was shown. As a result the best azides samples could be selected [4].

Treatment of polyethylene and other polymers surfaces by sulfamide azides solutions caused after UV-exposure bioactive nanoclusters formation on them. Such surface photomodification of polymeric films by azides containing sulfamide groups have been studied by different methods. Pentazadienes which contain five nitrogen atoms are also radical-forming agents and can decompose on three radicals and a molecule of nitrogen in photolysis. These compounds also can be used as photoinitiators of the radical polymerization [5].



By the action of pentazadienes in solutions on polymeric surfaces mixed clusters of different nature can be formed on illumination.

Biocide properties of films with sulfamide moieties or nanoclusters on the surface were tested and proved.

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THE ELECTRONIC EXCITATIONS ENERGY TRANSFER IN THE DNA. THE NATURE OF THE TRIPLET EXCITATIONS CAPTURING CENTRES

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It is known the deoxyribonucleic acid (DNA) is the vitally important biological macromolecule that functionally acts in the processes of the transfer, storing and realization of genetic information in every living creature. But until now the nature of the electronic processes in the DNA was not described completely.

The main aim of the present work is the investigation of the luminescence nature and electronic excitation transfer in the DNA macromolecule. The optical absorption, fluorescence and phosphorescence of the DNA, oligonucleotide

d(CCCGGGTTTAAA), double-stranded polynucleotide poly(dAdT)₂ and the low molecular model compounds of them (dGMP, dAMP, dCMP and dTMP) were examined. The system of energy levels and electronic processes in the DNA and d(CCCGGGTTTAAA) (specially designed and synthesized) were analyzed. It was shown the absorbing centers in the DNA macromolecules and d(CCCGGGTTTAAA) are the basic groups. Fluorescence of the DNA and d(CCCGGGTTTAAA) is connected with sum of fluorescence emissions of dGMP and dCMP that have the lowest singlet levels. To the other hand, phosphorescence of the DNA and d(CCCGGGTTTAAA) (due to migration of the electronic excitations) is close to emission of other type centers. The nature of these centers was found by comparing of the DNA, d(CCCGGGTTTAAA), poly(dAdT)₂, d(ATC) and d(AT) (specially designed and synthesized) phosphorescence spectra.

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PHOTOINDUCED ELECTRON TRANSFER IN FULLERENE BASED DONOR-ACCEPTOR COMPOUNDS

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A series of molecular crystals of fullerenes with various organic donors with neutral ground state has been obtained. Electron transfer in these compounds induced by photoexcitation has been studied by LESR- and RYDMR-spectroscopy and the possibility of charge separation has been established [1-2].

Photoconductivity and the effect of magnetic field ($B_0 < 1$ T) on photoconductivity have been studied for the first time in single crystals of layered donor-acceptor complexes of fullerene C₆₀ with tetrabenzyl-*p*-phenylenediamine (TBPDA·(C₆₀)₂), tetrabenzoz(1,2-bis[4H-thiopyran-4-ylidene]ethene) (Bz₄BTPE·C₆₀) [3], and metal dithiocarbamates, (M= Cu, Co [M(dedtc)₂]₂·C₆₀) [4]. A spin mechanism of free charge carrier generation in magnetic field was established. It has been shown that direct charge transfer from donor molecules to acceptor C₆₀ ones and photoexcitation of chromophore donor component contribute mainly to the generation of free charge carriers in fullerene complexes.

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MODIFICATION OF DNA MOLECULES FOR NONLINEAR OPTICAL APPLICATIONS.

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Nucleic acids and their derivatives attract the much attention of researchers due to their biological role. At the same time DNA, which has charge migration is a subject of interest for current physics study particularly for optoelectronics applications. The modified DNA are very promising candidate for application of molecular optics.

It is well known that the purified DNA is dissolved only in water. Therefore, we performed additional processing in order to make DNA more suitable for optoelectronics device fabrication with better optical quality.

We propose purified DNA in water with a cationic surfactant complex and also as thin films, in order to achieve new nanocomposites based on modified DNA for NLO compounds. The DNA-lipid complex is insoluble in aqueous solutions, but is soluble in most organic media.

In this work, we will present recent results of our studies concerning linear and non-linear optical properties of modified DNA. We studied these materials by

using the UV-VIS spectroscopy and different characterizations techniques of non-linear optics as like third harmonic generation (THG), degenerate four wave mixing (DFWM), electro optics effects. Comparative studies of the third-order optical susceptibilities will be also given.

PHOTOPROCESSES IN NEW PSORALEN SENSITIZERS

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Coumarin and its derivatives have been extensively studied due to their commercial applications in several fields. They possess excellent biological activity, such as anticancer and anticoagulant activity [1]. Moreover, this series of compounds has outstanding optical properties, including an extended spectral range, superior photostability and good solubility in common solvents. So these compounds are widely used as laser dyes [2–3], nonlinear optical chromophores, fluorescent whiteners [4], as well as fluorescent labels and probes for physiological measurement [5–8].

The quantum chemistry method of intermediate neglect of differential overlap (INDO) with spectroscopic parameterization [9] is used to study the electronic processes and spectral-luminescence properties of psoralen photosensitizer. The experimental investigation was carried out using SM-2203 spectrofluorimeter.

During carrying out of calculation spectra of absorption from the ground and excited states, rate constants have been received. The experimental and theoretical wavelengths corresponding maxima of absorption, coefficient of extinction was obtained. Calculated data for the first band were well agreed with available experimental data.

The special attention is given to studying of spectra of absorption from the excited states which are extremely informative from the point of view of data receiving about a structure of energy levels and the photoprocesses proceeding with participation of such states.

Theoretical spectra of absorption from the excited states for investigated molecules have been received. The calculated data are well agreed with experiment.

Research of spectral-luminescent properties of furocoumarins does more purposeful search new photosensitizers for various applications, first of all for bio- and photomedicine.

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THE PECULIARITIES OF TRANSIENT CURRENTS IN LIQUID HYDROCARBONS

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The transient currents in liquid hydrocarbons depend on nature and purity of liquid, on electrode materials and state of their surfaces, on intensity and time interval application of electric field, on temperature and other factors. The review of the most known works on transient currents in liquid hydrocarbons has been presented.

When a dc voltage is applied to the cells with liquid hydrocarbon the charging currents are flowing. By analyses of charging currents as a function of time it is possible to classify these characteristics into three categories: (i) decreasing in time (toluene, hexane and another liquid hydrocarbons); (ii) not changing in time (hydrocarbon oils with conducting particles) and (iii) increasing

in time (pure benzene). The nature of these current-time characteristics is explained by different electrical properties of the investigated liquid hydrocarbons and by the peculiarities of the experimental conditions.

The additional information about conduction in liquid hydrocarbons can be obtained from investigation of the discharging currents [1]. Usually a discharging (or depolarization) current flows in the opposite direction of the charging current and equals in magnitude to the charging one (linear case). An anomalous behavior of the discharging current is observed in dimethylsiloxane where the discharging current remains negative for low electric fields, and this current becomes positive for higher fields after an initial time interval. The transition of the discharging current from negative to positive is known as the transition from a heteropolar to homopolar current. The similar transition of the discharging current was observed in silicone oil AP 100 (Walker Chemie GmbH). The investigation of the discharging currents in liquid hydrocarbons is a good instrument to analyze the state of these liquids after initial action of the electric field.

For more detailed information about conduction processes in liquid hydrocarbons the investigation of the reversal currents can be used [2] and different cases of these currents are discussed. One or two peaks were observed in reversal currents in toluene and carbon tetrachloride. The carrier charge mobility was evaluated from the measurements of the time interval for reversal current maximum.

The combined investigation of charging, discharging and reversal currents is a useful method which allows to study the nature and peculiarities of conduction in liquid hydrocarbons [3,4,5] and liquid crystals [4].

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THE STRUCTURE OF SOL-GEL BIOACTIVE POWDERS OF CALCIUM HYDROXYAPATITE

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One of active restorers of a bone is calcium hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (Ca-HAP). It is possible to use this material in a state of powders and granules for substitution of defective segments of bone tissues of the person and animal. The key problem of bioactivity consists of formation of such structural selforganization, which conduced to interaction of a physiological liquid with implant for a stimulation of a metabolism in a defective zone. It can achieve by obtaining nano- and microporosity in powders and granules for realisation the capillary effect of organic saturation.

For obtaining of pure, homogeneous nano- and micropowders Ca-HAP was used the sol - gel technology based on the synthesis of molecules HAP in solutions of calcium and ammonium salts and phosphoric acids. The density of reactants in a reaction mixture, temperature, time of reaction, pH of solution, type of the medium (reduction, oxidative or neutral) for efficient control this multiparameter process were varied. These factors determine a degree of structural perfection and physicochemical properties Ca-HAP.

The aim of this investigation is the search of parameters of sol - gel synthesis for obtaining of high porous Ca-HAP powders, the research of the nucleation and growth mechanism of a crystalline phase with high specific surface. The structure of particles on the different stages of synthesis: transformation of sol in a gel, condensation of a deposit, waters flushing, drying, and annealing - was studied by the transmission electron microscopy and microdiffraction.

The powder consists of spherical and long particles of size from 50 up to 150 nm, which by annealing can be aggregated in granules. It was analysed the composite absorption and diffraction contrast of an electron micrographes of the structure at different stages of synthesis and was investigated the growth mechanism of a crystalline phase Ca-HAP obtained by a sol - gel method.

The colloidal-chemical genesis of calcium hydroxyapatite structure begins with formation of amorphous particles, then occur clusters of a crystalline phase in an amorphous matrix and this process ends with aggregate (coalescence or coagulation) of particles Ca-HAP. To obtaining of powders with a high specific surface of the order $100 \text{ m}^2/\text{g}$ the activation of coalescence is undesirable. The necessary conditions arise at low temperatures 120-150°C, which is insufficient for a sintering of particles therefore a high specific surface in polycrystalline granule form. The biological activity of a calcium hydroxyapatite implant and high velocity of regeneration of bone occur due to the high nano- and microporosity.

BIOLOGICAL EFFECTS OF C₆₀ FULLERENES *IN VITRO* AND IN THE MODEL SYSTEMS

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The new allotropic form of carbon – C₆₀ fullerenes, in which the carbon atoms form the high stable spherical-like structure with unique physical and chemical properties [1], are shown to exhibit the biological activity *in vitro* [2]. The biological effect of C₆₀ fullerenes to a great extent depends on the irradiation treatment. As a result of energy absorption the C₆₀ fullerenes are converted to the excited triplet state and initiate the reactions of free radical oxidation. In the present paper the study of water-soluble C₆₀ fullerene effects on the cell viability and DNA structure after the light and X-ray irradiation was done. The electron-transport chain activity measured by the MTT test was shown to be decrease after the irradiation of 10⁻⁵ M C₆₀ fullerene – containing suspension of Ehrlich ascite cells, but not of rat thymocytes. The intensification of DNA fragmentation and lipid peroxidation in the irradiated C₆₀ fullerene – containing cell suspension were also detected.

The experiments on the planar lipid bilayer membranes and voltage-clamp recordings of the transmembrane current show that membrane conductance after 10⁻⁵ M C₆₀ fullerene addition is significantly increased although the increase is transient. C₆₀ fullerenes do not penetrate through the lipid bilayer, but are hold inside the lipid bilayer for a relatively long period of time.

The ways of excited C₆₀ fullerene effects through the singlet oxygen or superoxide anion formation [3] and its possible application for the photodynamic therapy are discussed.

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THE SYNTHETIC AND BIOLOGICAL FUNCTIONAL COMPOUNDS WITH THE DIRECT EXCITONS CONDUCTIVITY FOR NANOELECTRONIC DEVICES

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Recently in the modern nanoelectronics world the problem of development of the electronics basic elementary functional units of molecular (nano-) sizes sharply appears and requires to search for new technological solutions. In this connection organic π -electron-containing functional macromolecules with known predetermined energy structure and, as the result, the properties of predicted one-way exciton conductivity have been proposed as the basic elements for nanoelectronics. The combining of such elements in some logic structures is the way to creation of the advanced technology nanoelectronic devices.

The aim of the present paper is the design, synthesis and investigations of the special functional compounds containing several (up to 12) π -electron systems. The spectral investigations results of a number synthetic natural-nucleotides-containing compounds are compared with the results obtained on the deoxyribonucleic acid (DNA). The predicted processes of the direct triplet electronic excitations transfer existence in all the specially designed and synthesized functional compounds under selective photon excitation were established. This fact gives the possibility to propose these compounds to be used for nanotechnology devices. The computer simulations of the electronic excitation passing through the functional macromolecule (that consists of 12 links and that is

close to real macromolecule) were done. These calculations take into account the reverse exciton currents and the multipath excitation energy migration.

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TWO-PHOTON EXCITED LUMINESCENT STYRYL DYES AS THE PROBES FOR THE DNA DETECTION AND IMAGING. PHOTOSTABILITY AND PHOTOTOXIC INFLUENCE ON THE DNA

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It is known one of the most reliable methods of the DNA and other biological objects detection for biomedical investigations as well as for applied medicine is the use of fluorescent dye probes. In these cases the dyes with quantum yield that greatly increases under interaction of these dyes with biological objects are used. Recently the papers that show the phototoxicity of some of such type dyes (for example, TO-TO) have appeared.

In the present paper the spectral methods of fluorescent dye probes phototoxicity (or, contrary, photostability) phenomenon spectral investigation were proposed. The optical absorption spectra of the samples of the newest investigated two-photon excited styryl dyes and the systems DNA+dye were measured under the irradiation of these samples by visible light of Hg-lamp (DRT-1000) for 1-9 hours. As it is well known one of the phototoxicity manifestation is the damage of a biological object (in our case – the DNA) under direct excitation of the fluorescent probe which contact with this object. It is worth to note the DNA absorption band connected with the first electronic transition (at 260 nm) is located far from the same band of majority of dyes used in our investigations (400-500 nm). This fact and the fact that the value of optical density of the dyes absorption band connected with the second electronic transition (located at

~260 nm) is much less than correspondent value of the DNA band gives the possibility to study the behavior dynamics of the absorption bands optical density almost independently for a dye and for the DNA. In our experiments optical density $D(t)$ in mentioned above wavelength region of the DNA+dye solutions increased under irradiation in the first absorption band of the dye that was evidence of the DNA basic groups photochemical modification. The dynamics of $D(t)$ was not monotonous. The results of the investigations carried out on a number of dyes were analyzed and discussed. It was shown the DNA first absorption band for the system of Dst-MdO dye bound to the DNA decreased under irradiation in the first absorption band of Dst-MdO that was evidence of the DNA photodamage. The value of D of optical absorption band of the DNA in Di-Styr-24 dye presence increased during time of irradiation. The versions of possible phototoxicity (and, contrary, photostability) mechanisms are proposed.

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OPTICAL TRANSITIONS IN BIOLOGICAL STRUCTURES INDUCED BY UV-IRRADIATION. SPR OBSERVATION

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UV-radiation is an important factor affecting living nature. Except photosynthetic activity it play great role in apoptosys processes, radiative damage of

nucleic acids, gene mutation and other. So changes in biologically active ultraviolet radiation reaching the Earth's surface all time are under control [1]. There are number of publications in the biological literature of the last years which have been devoted to the problem of the influence of UV-B radiation on photosynthetic processes in vegetative plants in

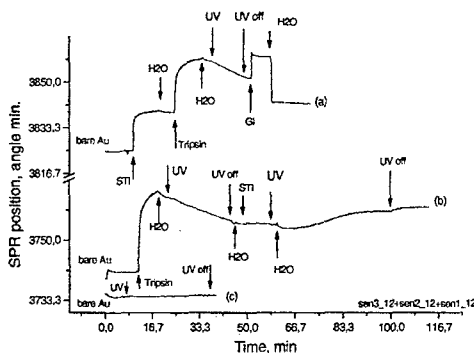


Fig.1. The SPR sensogrammes for reaction of biospecific binding between pair STI-trypsin for bare gold surface (curve c) and for reverse specific reaction (curves a,b).

viewpoint of transgenic engineering for creation of novel sorts of plants [2-3]. However, all these researches were conducted by biological methods without investigation of mechanisms of biomolecular interactions. It is worth to note only work [3] where authors proposed a molecular model of interaction of two proteins which could be used for recognizing of the molecular mechanism of the UV-B radiation influence on inter-protein binding.

We have examined the interactions of soybean trypsin inhibitor (STI) and trypsin under UV-irradiation by electrochemical surface plasmon resonance (ESPR) to gain a better understanding of structure, kinetics and thermodynamics. UV-irradiation plays an essential role in the biochemical processes in live nature due to high-energy photons, which are able to change structural properties of biomolecules. With SPR we found a reduction in effective refractive index trypsin layer as a consequence of UV irradiation. At the same conditions, no noticeable changes for refractive index of STI layer was detected. Because UV irradiation leads to conformational changes of some biomolecules, we do not observed any specific binding of STI to UV-damaged trypsin. At the same time, after UV-irradiation of STI no significant changes in specific binding of trypsin was observed (Fig.1), that can be explained by UV-degradation of active centre of trypsin and more stable molecular conformation of STI.

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